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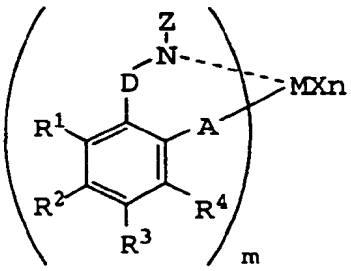
## (54) Olefin polymerization catalyst and polymerization process

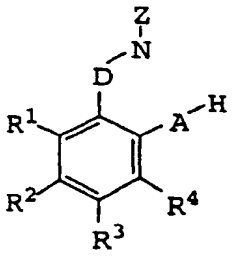
(57) An olefin polymerization catalyst having an excellent polymerization activity and an olefin polymerization process using the catalyst are disclosed. The olefin polymerization catalyst comprises (A) a transition metal compound represented by, for example, the following formula (I) and optionally (B) at least one compound selected from an organometallic compound, an organoaluminum oxy-compound and a compound which reacts with the transition metal compound (A) to from an ion pair;




...(I)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table; m is an integer of 1 to 6; A is -O-, -S-, -Se- or -N(R5)-; D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$ or the like; Z is $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$, $=NR^{17}$ or the like; $R^1$ to $R^{17}$ are each H, a hydrocarbon group or the like; n is a number satisfying a valence of M; and X is halogen, a hydrocarbon group or the like.

EP 0 950 667 A2



... (a)

wherein A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$,
D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-,
Z is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{17}$, and
$R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring;

$$MXk \qquad (e)$$

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,
k is a number satisfying a valence of M, and
X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group, and when k is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**[0007]** The second olefin polymerisation catalyst according to the invention comprises:

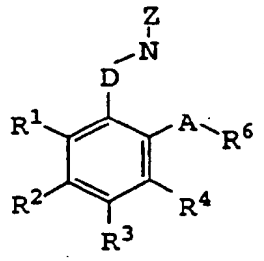
(A) a transition metal compound which is obtained by bond-forming reaction of a compound represented by the following formula (b) with a metallic compound represented by the above formula (e) and in which the molar ratio of ligands to metal atoms is in the range of 1 to 6, said ligands being derived from the compound of the formula (b) and bonded to said metal atoms, and optionally
(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair;

**[0009]** The fourth olefin polymerization catalyst according to the invention comprises:

(A) a transition metal compound which is obtained by bond-forming reaction of a compound represented by the following formula (d) with a metallic compound represented by the above formula (e) and in which the molar ratio of ligands to metal atoms is in the range of 1 to 6, said ligands being derived from the compound of the formula (d) and bonded to said metal atoms, and optionally
(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair;



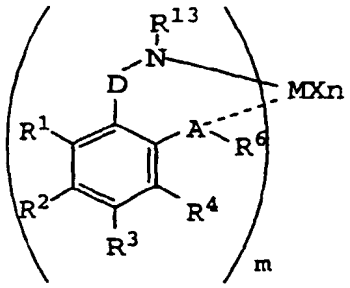
... (d)

wherein A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$,
D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-,
Z is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{17}$, and
$R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring.

**[0010]** The fifth olefin polymerization catalyst according to the invention comprises:

(A) a transition metal compound represented by the following formula (I), and optionally
(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair;



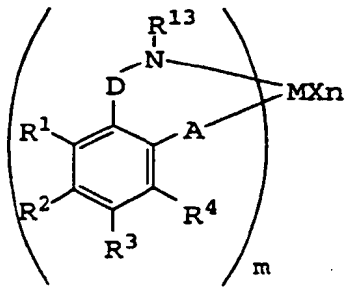
...(II)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,
m is an integer of 1 to 6.
A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$,
D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, $-CO-$ or $-S-$,
$R^1$ to $R^{13}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, two or more of them may be bonded to each other to form a ring, and when m is a plural number, one group of $R^1$ to $R^{13}$ contained in one ligand and one group of $R^1$ to $R^{13}$ contained in other ligands may be bonded, and $R^1$s, $R^2$s, $R^3$s, $R^4$s, $R^5$s, $R^6$s, $R^7$s, $R^8$s, $R^9$s, $R^{10}$s, $R^{11}$s, $R^{12}$s, or $R^{13}$s may be the same or different, respectively,
n is a number satisfying a valence of M, and
X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group, and when n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**[0012]** The seventh olefin polymerization catalyst according to the invention comprises:

(A) a transition metal compound represented by the following formula (III), and optionally
(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair;



...(III)

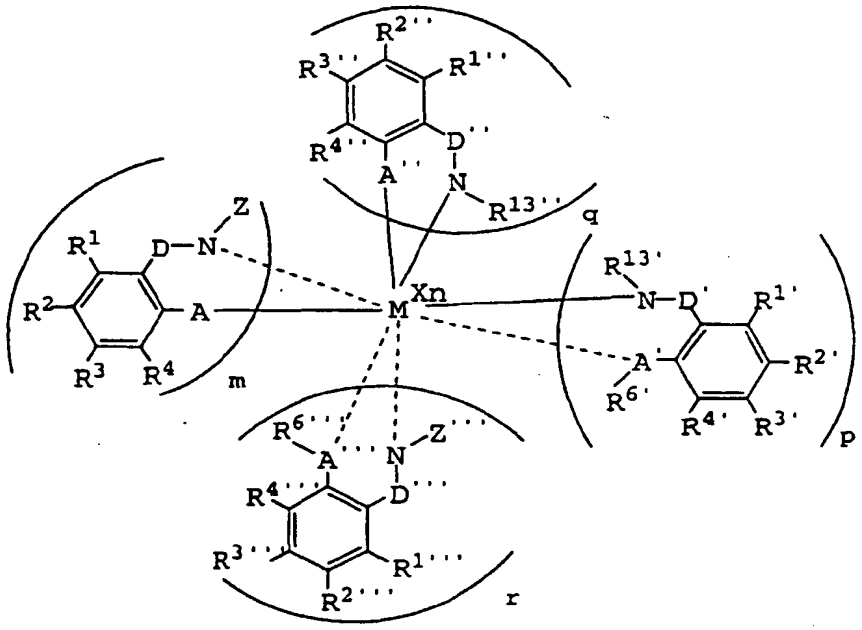
wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

germanium-containing group or a tin-containing group, and when n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**[0014]** The ninth olefin polymerization catalyst according to the invention comprises:

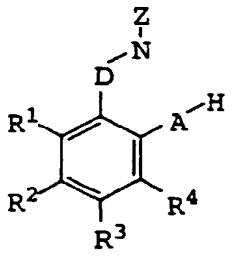
(A) a transition metal compound represented by the following formula (V), and optionally
(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair;



. . . (V)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,
m is an integer of 0 to 6, p is an integer of 0 to 6, q is an integer of 0 to 3, r is an integer of 0 to 6, three or more of them is not 0 at the same time, and they are numbers satisfying the conditions of $m+p+q+r \leq 6$ and $m+p+2q \leq 6$,
A, A', A" and A"' may be the same or different and are each an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$ (or $-R^{5'}$, $-R^{5''}$ and $-R^{5'''}$ correspondingly to A', A" and A"', respectively, and the same shall apply hereinafter),
D, D', D" and D"' may be the same or different and are each $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-,
Z and Z"' may be the same or different and each of them is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{17}$,
$R^1$ to $R^{17}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ may be the same or different, they are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, two or more of them may be bonded to each other to form a ring, and in case of $m+p+q+r \geq 2$, one group of $R^1$ to $R^{16}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ contained in one ligand and one group of $R^1$ to $R^{17}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ contained in other ligands may be bonded, and $R^1$, $R^{1'}$, $R^{1''}$ and $R^{1'''}$, $R^2$, $R^{2'}$, $R^{2''}$ and $R^{2'''}$, $R^3$, $R^{3'}$, $R^{3''}$ and $R^{3'''}$, $R^4$, $R^{4'}$, $R^{4''}$ and $R^{4'''}$, $R^5$, $R^{5'}$, $R^{5''}$ and $R^{5'''}$, $R^6$, $R^{6'}$, $R^{6''}$ and $R^{6'''}$, $R^7$, $R^{7'}$, $R^{7''}$ and $R^{7'''}$, $R^8$, $R^{8'}$, $R^{8''}$ and $R^{8'''}$, $R^9$, $R^{9'}$, $R^{9''}$ and $R^{9'''}$, $R^{10}$, $R^{10'}$, $R^{10''}$ and $R^{10'''}$, $R^{11}$, $R^{11'}$, $R^{11''}$ and $R^{11'''}$, $R^{12}$, $R^{12'}$, $R^{12''}$ and $R^{12'''}$, $R^{13}$, $R^{13'}$



... (a)

**[0025]** In the formula (a), A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$.

**[0026]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and $-C(R^7)(R^8)-$ is particularly preferable.

**[0027]** Z is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{16}$. (The symbols "-" and "=" mean a single bond and a double bond, respectively. The same shall apply hereinafter.)

**[0028]** $R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring. However, it is preferable that $R^{12}$ or $R^{13}$ is an atom or a group other than a hydrogen atom.

**[0029]** $R^1$ to $R^{17}$ may be the same or different and are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, an aluminum-containing group, a sulfur-containing group or a silicon-containing group.

**[0030]** More specifically, $R^1$ to $R^{17}$ are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonato ester group, a sulfonamido group, a cyano group, a nitro group, a carboxyl group, a sulfo group, a mercapto group, an aluminum-containing group or a hydroxyl group. However, it is preferable that $R^{13}$ or $R^{14}$ is an atom or a group other than a hydrogen atom.

**[0031]** $R^1$ to $R^4$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group or a hydrocarbon-substituted siloxy group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or a hydrocarbon-substituted silyl group.

**[0032]** Also, $R^5$ to $R^{17}$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group or an aluminum-containing group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or an aluminum-containing group.

**[0033]** The halogen atoms include fluorine, chlorine, bromine and iodine.

**[0034]** Examples of the hydrocarbon groups include straight-chain or branched alkyl groups of 1 to 30 carbon atoms, pref rably 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl and n-hexyl; straight-chain or branched alkenyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atoms, such as vinyl, allyl and isopropenyl; straight-chain or branched alkynyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atoms, such as ethynyl and propargyl; cyclic saturated hydrocarbon groups of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and adamantyl; cyclic unsaturated hydrocarbon groups of 5 to 30 carbon atoms, such as cyclopentadienyl, indenyl and fluorenyl; aryl groups of 6 to 30 carbon atoms, preferably 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl, terphenyl, phenanthryl and anthracenyl; and alkyl-substituted aryl groups, such as tolyl, isopropylphenyl, t-butylphenyl, dimethylphenyl and di-t-butylphenyl.

**[0035]** In the above hydrocarbon groups, hydrogen may be replaced with a halogen atom, and examples of these halogenated hydrocarbon groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, include trifluoromethyl, pentafluorophenyl and chlorophenyl.

**[0036]** In the above hydrocarbon groups, hydrogen may also be replaced with another hydrocarbon group, and examples of these aryl-substituted alkyl groups include benzyl and cumyl.

**[0043]** Examples of the aluminum-containing groups include alkyl-substituted aluminum, aryl-substituted aluminum, halogenated aluminum and alkyl-substituted halogenated aluminum. Specifically, there can be mentioned alkyl-substituted aluminum, such as $(Et)_2Al$-, $(iPr)_2Al$-, $(iBu)_2Al$-, $(Et)_3Al$, $(iPr)_3Al$ and $(iBu)_3Al$; aryl-substituted aluminum, such as $(C_6H_5)_2Al$-; halogenated aluminum, such as $AlCl_2$- and $AlCl_3$; and alkyl-substituted halogenated aluminum, such as (Et)AlCl- and (iBu)AlCl-. Of these, the tri-substituted aluminum may be in a state of coordinate bond. The symbols "Et", "iPr" and "iBu" used herein denote an ethyl group, an isopropyl group and an isobutyl group, respectively.

**[0044]** Examples of the silicon-containing groups include a silyl group, a siloxy group, a hydrocarbon-substituted silyl group and a hydrocarbon-substituted siloxy group. Particular examples of the hydrocarbon-substituted silyl groups include methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl, triphenylsilyl, dimethylphenylsilyl, dimethyl-t-butylsilyl and dimethyl(pentafluorophenyl)silyl. Of these, preferable are methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, dimethylphenylsilyl and triphenylsilyl. Particularly preferable are trimethylsilyl, triethylsilyl, triphenylsilyl and dimethylphenylsilyl. Particular examples of the hydrocarbon-substituted siloxy groups include trimethylsiloxy.

**[0045]** Examples of the germanium-containing groups or the tin-containing groups include groups wherein silicon is replaced with germanium or tin in the above-exemplified silicon-containing groups.

**[0046]** The above examples of the groups $R^1$ to $R^{17}$ are more specifically described below.

**[0047]** Of the oxygen-containing groups, preferred examples of the alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and tert-butoxy; preferred examples of the aryloxy groups include phenoxy and 2,6-dimethylphenoxy, 2,4,6-trimethylphenoxy; preferred examples of the acyl groups include formyl, acetyl, benzoyl, p-chlorobenzoyl and p-methoxybenzoyl; and preferred examples of the ester groups include acetyloxy, benzoyloxy, methoxycarbonyl, phenoxycarbonyl and p-chlorophenoxycarbonyl.

**[0048]** Of the nitrogen-containing groups, preferred examples of the amido groups include acetamido, N-methylacetamido and N-methylbenzamido; preferred examples of the amino groups include dimethylamino, ethylmethylamino and diphenylamino; preferred examples of the imido groups include acetimide and benzimide; and preferred examples of the imino groups include methylimino, ethylimino, propylimino, butylimino and phenylimino.

**[0049]** Of the sulfur containing groups, preferred examples of the alkylthio groups include methylthio and ethylthio; preferred examples of the arylthio groups include phenylthio, methylphenylthio and naphthylthio; preferred examples of the thioester groups include acetylthio, benzoylthio, methylthiocarbonyl and phenylthiocarbonyl; preferred examples of sulfonato ester groups include methylsulfonato, ethylsulfonato and phenylsulfonato; and preferred examples of the sulfonamido groups include phenylsulfonamido, N-methylsulfonamide and N-methyl-p-toluenesulfonamide.

**[0050]** Two or more groups of $R^1$ to $R^{17}$, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom. These rings may further have a substituent.

**[0051]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-.

**[0052]** Preferred examples of $-C(R^7)(R^8)-$ include divalent hydrocarbon groups of 1 to 20 carbon atoms, such as alkylene groups (e.g., methylene, dimethylmethylene, 1,2-ethylene, dimethyl-1,2-ethylene, 1,3-trimethylene, 1,4-tetramethylene, 1,2-cyclohexylene and 1,4-cyclohexylene) and arylalkylene groups (e.g., diphenylmethylene and diphenyl-1,2-ethylene). Of these, methylene is preferable.

**[0053]** Preferred examples of $-Si(R^9)(R^{10})-$ include divalent silicon-containing groups, such as alkylsilylene, alkylarylsilylene and arylsilylene groups (e.g., methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methyphenylsilylene, diphenylsilylene, di(p-tolyl)silylene and di(p-chlorophenyl)silylene), and alkyldisilylene, alkylaryldisilylene and aryldisilylene groups (e.g., tetramethyl-1,2-disilylene and tetraphenyl-1,2-disilylene).

**[0054]** $R^{11}$ is preferably an oxygen-containing group, more preferably an alkoxy group, an aryloxy group or an arylalkoxy group, particularly preferably methoxy or phenoxy.

**[0055]** The metallic compound to be reacted with the compound of the formula (a) is represented by the following formula (e):

$$MXk \qquad (e)$$

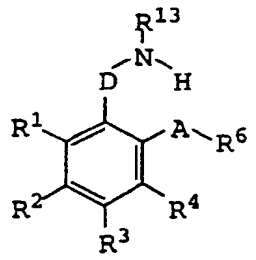
**[0056]** In the formula (e), M is a transition metal atom of Group 3 (including lanthanoid) to Group 11 of the periodic table, preferably a metal atom of Group 3 (including lanthanoid) to Group 10, more preferably a metal atom of Group 3 to Group 5 and Group 8 to Group 10, particularly preferably a metal atom of Group 4 or Group 5. Examples of the metal atoms include scandium, yttrium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, cobalt, rhodium, nickel and palladium. Of these, preferable are scandium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt, rhodium, nickel and palladium. More preferable are titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt and rhodium. Particularly preferable are titanium, zirconium and hafnium.

**[0073]** When k is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**[0074]** Examples of the metallic compounds MXk of the formula (e) include $TiCl_3$, $TiCl_4$, $TiBr_3$, $TiBr_4$, $Ti(CH_2C_6H_5)_4$, $Ti(NMe_3)_4$, $ZrCl_4$, $ZrBr_4$, $Zr(CH_2C_6H_5)_4$, $Zr(NMe_3)_4$, $HfBr_4$, $HfCl_4$, $VCl_4$, $VCl_5$, $VBr_4$, $VBr_5$, $NbCl_5$, $NbBr_5$, $TaCl_5$, $TaBr_4$, $Ti(acac)_3$, $FeCl_2$, $FeCl_3$, $FeBr_2$, $FeBr_3$, $CoCl_2$, $CoCl_3$, $CoBr_2$, $CoBr_3$, $RhCl_2$, $RhCl_3$, $RhBr_2$, $RhBr_3$, $NiCl_2$, $NiBr_2$, $PdCl_2$, $PdBr_2$, and complexes of these compounds and THF (tetrahydrofuran), acetonitrile or diethyl ether.

**[0075]** In the transition metal compound obtained by reacting the compound represented by the formula (a) with the metallic compound represented by the formula (e), the molar ratio of the ligands to the metal atoms is in the range of preferably 1 to 6, more preferably 1 to 4, particuraly preferably 1 or 2, said ligands being derived from the compound of the formula (a) and bonded to the metal atoms. The molar ratio in the reaction product can be confirmed by, for example, elemental analysis, X-ray crystal structure analysis and analyses of mass spectrum, NMR and IR of the isolated transition metal compound.

**[0076]** The second transition metal compound for use in the invention is obtained by bond-forming reaction of a compound represented by the following formula (b) with the metallic compound represented by the aforesaid formula (e):



... (b)

**[0077]** In the formula (b), A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$.

**[0078]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and $-C(R^7)(R^8)-$ is particularly preferable.

**[0079]** $R^1$ to $R^{13}$ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring. It is preferable that $R^6$ is an atom or a group other than a hydrogen atom.

**[0080]** $R^1$ to $R^{13}$ may be the same or different and are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, an aluminum-containing group, a sulfur-containing group or a silicon-containing group.

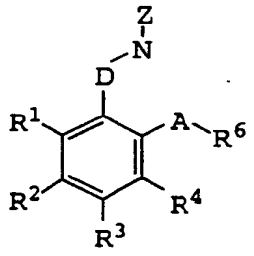
**[0081]** More specifically, it is preferable that $R^1$ to $R^{13}$ is a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonato ester group, a sulfonamido group, a cyano group, a nitro group, a carboxyl group, a sulfo group, a mercapto group, an aluminum-containing group or a hydroxy group.

**[0082]** $R^1$ to $R^4$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group or a hydrocarbon-substituted siloxy group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or a hydrocarbon-substituted silyl group.

**[0083]** Also, $R^5$ to $R^{17}$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group or an aluminum-containing group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or an aluminum-containing group.

**[0084]** Examples of the groups $R^1$ to $R^{13}$ include the same groups as previously exemplified with respect to $R^1$ to $R^{17}$ in the formula (a).

**[0085]** Examples of the groups D include the same groups as previously exemplified with respect to D in the formula (a).



. . . (d)

**[0099]** In the formula (d), A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$.

**[0100]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and $-C(R^7)(R^8)-$ is particularly preferable.

**[0101]** Z is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{16}$.

**[0102]** $R^1$ to $R^{17}$ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring. It is preferable that any one of $R^6$, $R^{13}$ and $R^{14}$ is an atom or a group other than a hydrogen atom.

**[0103]** $R^1$ to $R^{17}$ may be the same or different and are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, an aluminum-containing group, a sulfur-containing group or a silicon-containing group.

**[0104]** More specifically, it is preferable that $R^1$ to $R^{17}$ is a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonato ester group, a sulfonamido group, a cyano group, a nitro group, a carboxyl group, a sulfo group, a mercapto group or a hydroxy group. It is preferable that $R^{13}$ or $R^{14}$ is an atom or a group other than a hydrogen atom.

**[0105]** $R^1$ to $R^4$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group or a hydrocarbon-substituted siloxy group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or a hydrocarbon-substituted silyl group.

**[0106]** Also, $R^5$ to $R^{17}$ are each preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group or an aluminum-containing group, and particularly preferably a hydrogen atom, a hydrocarbon group, a heterocyclic compound residual group or an aluminum-containing.

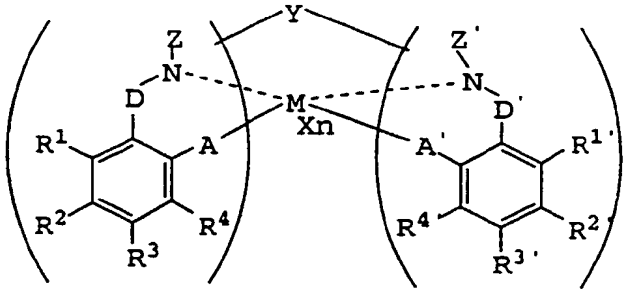
**[0107]** Examples of the groups indicated by $R^1$ to $R^{17}$ include the same groups as previously exemplified with respect to $R^1$ to $R^{17}$ in the formula (a).

**[0108]** Examples of the groups D include the same groups as previously exemplified with respect to D in the formula (a).

**[0109]** In the transition metal compound obtained by reacting the compound represented by the formula (d) with the metallic compound represented by the formula (e), the molar ratio of the ligands to the metal atoms is in the range of 1 to 6, preferably 1 to 4, more preferably 1 or 2, said ligands being derived from the compound of the formula (d) and bond d to the metal atoms.

**[0110]** There is no specific limitation on the bond-forming reaction of the compound represented by any of the formulas (a) to (d) with the metallic compound represented by the formula (e), and for example, the compound represented by any of the formulas (a) to (d) is per se allowed to react with the metallic compound of the formula (e), e.g., a transition metal halide or a transition metal alkylate, or the compound represented by any of the formulas (a) to (c) is allowed to react with a base to give an anion and the anion is allowed to react with the metallic compound of the formula (e), e.g., a transition metal halide or a transition metal alkylate, as described later.

**[0111]** The fifth transition metal compound for use in the invention is a compound represented by the following formula (I):



...(I-a)

**[0123]** In the formula (I-a), A, D, Z, $R^1$ to $R^{17}$, M and X are the same as A, D, Z, $R^1$ to $R^{17}$, M and X in the aforesaid formula (I), and A' may be the same as or different from A and is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^{5'}$. D' may be the same as or different from D and is $-C(R^{7'})(R^{8'})-$, $-Si(R^{9'})(R^{10'})-$, $-P(O)(R^{11'})-$, $-P(R^{12'})-$, -SO- or -S-. Of these, $-C(R^{7'})(R^{8'})-$ is preferable. Z' may be the same as or different from Z, is a bonding group of N and represents $-R^{13'}$ and $-R^{14'}$, $=C(R^{15'})R^{16'}$ or $=NR^{17'}$.

**[0124]** $R^{1'}$ to $R^{17'}$ have the same meanings as those of $R^1$ to $R^{17}$ in the formula (I), respectively, and they preferably are each the following group.

**[0125]** That is, $R^{1'}$ to $R^{17'}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of these atoms and groups include the same atoms and groups as previously descried with respect to $R^1$ to $R^{17}$ in the formula (a). However, it is preferable that $R^{13'}$ or $R^{14'}$ is an atom or a group other than a hydrogen atom. Two or more groups of $R^{1'}$ to $R^{17'}$, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom.

**[0126]** Y is a bonding group or a single bond for bonding at least one group selected from $R^1$ to $R^{17}$ to at least one group selected from $R^{1'}$ to $R^{17'}$. Although the bonding group is not specifically limited, it preferably has a structure wherein the main chain is constituted of 3 or more atoms, preferably 4 to 20 atoms, particularly preferably 4 to 10 atoms. The bonding group may have a substituent.

**[0127]** The bonding group Y can be a group containing at least one element selected from oxygen, sulfur, carbon, nitrogen, phosphorus, silicon, selenium, tin and boron. Examples of such groups include groups containing halogen atoms such as -O-, -S- and -Se-; nitrogen- or phosphorus-containing groups, such as -NH-, $-N(CH_3)_2-$, -PH- and $-P(CH_3)_2-$; hydrocarbon groups of 1 to 20 carbon atoms, such as $-CH_2-$, $-CH_2-CH_2-$ and $-C(CH_3)_2-$; residual groups of cyclic unsaturated hydrocarbons of 6 to 20 carbon atoms, such as benzene, naphthalene and anthracene; residual groups of heterocyclic compounds having 3 to 20 carbon atoms and containing hetero atoms, such as pyridine, quinoline, thiophene and furan; silicon-containing groups, such as $-SiH_2-$ and $-Si(CH_3)_2-$; tin-containing groups, such as $-SnH_2-$ and $-Sn(CH_3)_2-$; and boron-containing groups, such as -BH-, $-B(CH_3)-$ and -BF-. Y can also be a single bond.

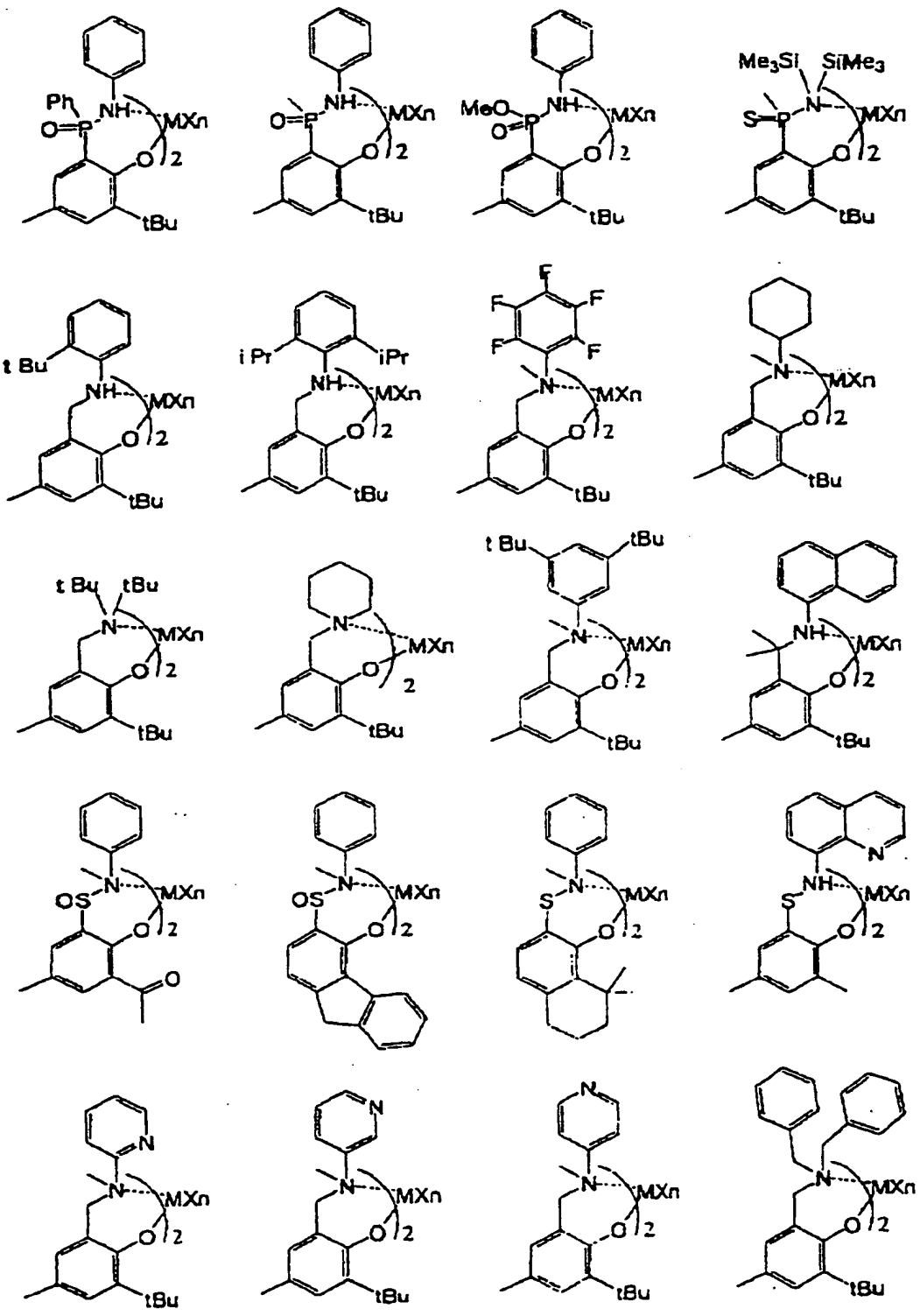
**[0128]** Examples of the transition metal compounds represented by the formula (I) are given below, but not limited thereto.

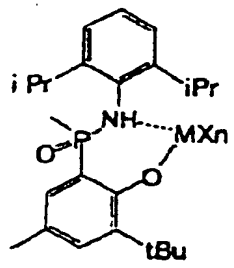
**[0129]** In the following examples, M is a transition metal atom of Group 3 to Group 11 of the periodic table, and particular examples of such metals include scandium, yttrium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, cobalt, rhodium, nickel and palladium. Of these, preferable are scandium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt, rhodium, nickel and palladium. More preferable are titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt and rhodium. Particularly preferable are titanium, zirconium and hafnium.

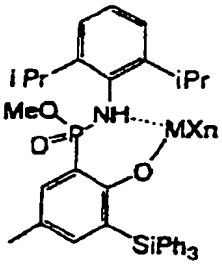
**[0130]** X is halogen such as Cl or Br, or an alkyl group such as methyl, but not limited thereto. When plural X are present, they may be the same or different.

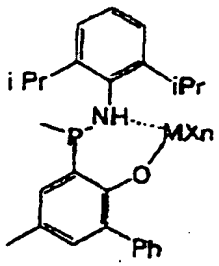
**[0131]** n is decided by a valence of the metal M. For example, when two monoanions are bonded to the metal, there can be mentioned n = 0 in case of a divalent metal, n = 1 in case of a trivalent metal, n = 2 in case of a tetravalent metal, and n = 3 in case of a pentavalent metal. More specifically, there can be mentioned n = 2 in case of Ti(IV), n = 2 in case of Zr(IV), and n = 2 in case of Hf(IV).

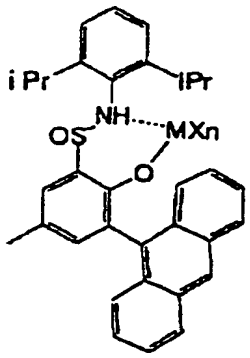
**[0132]** In the following examples, Me denotes methyl, Et denotes ethyl, iPr denotes i-propyl, tBu denotes tert-butyl, and Ph denotes phenyl.

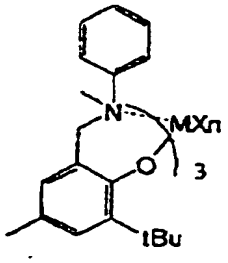


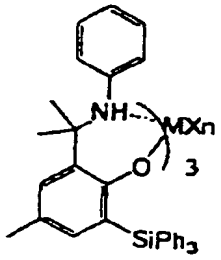


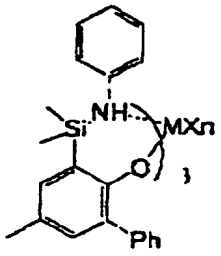



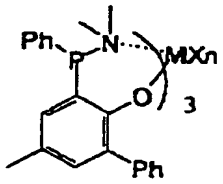



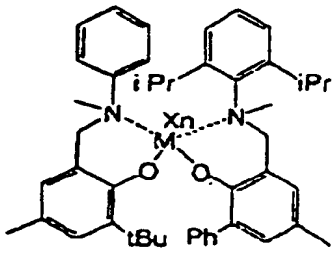



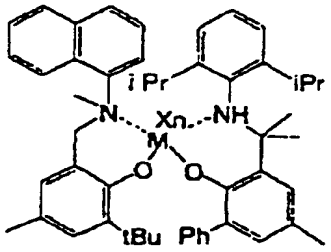



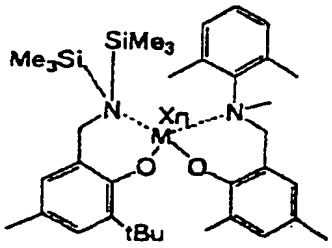



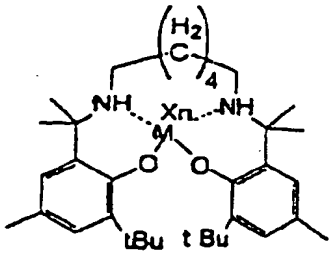



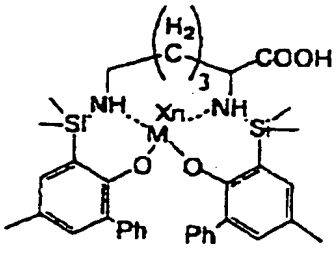



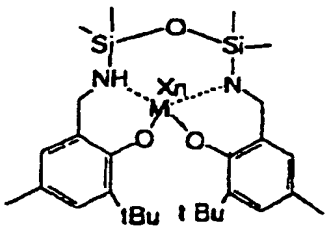



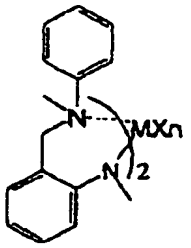



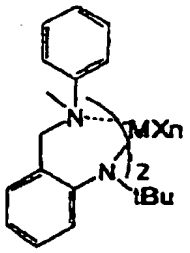



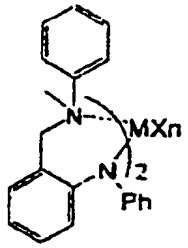



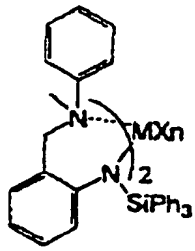



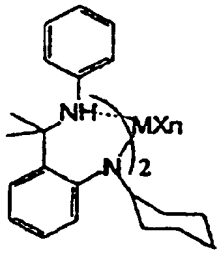



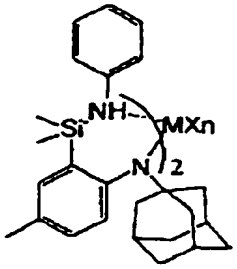


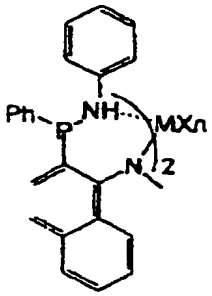



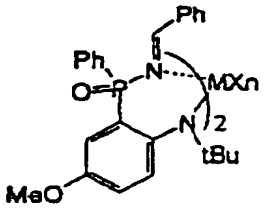



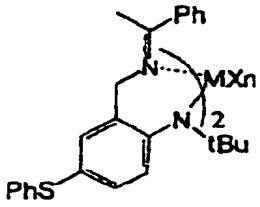



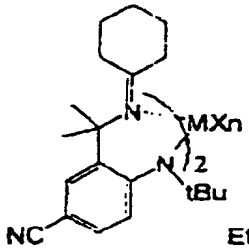



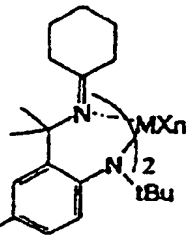



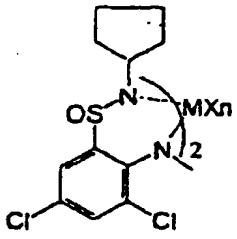



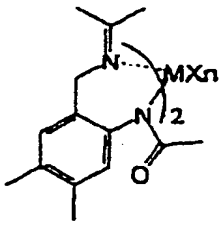



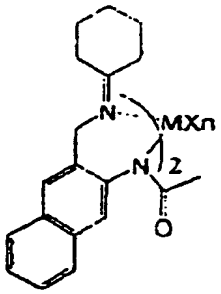



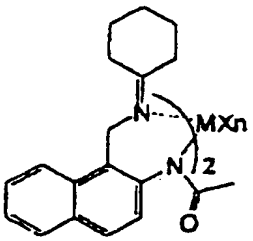



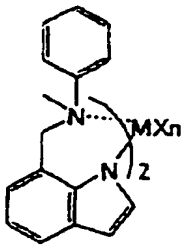



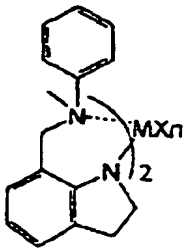



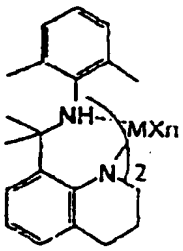



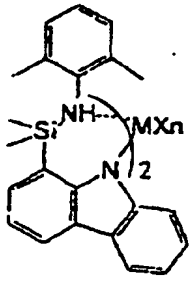



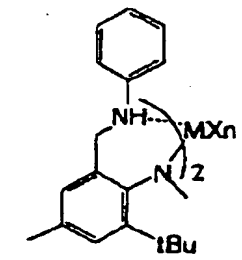



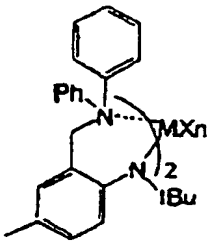



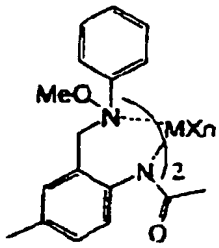



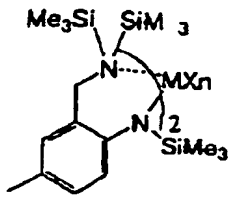



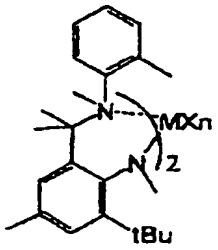



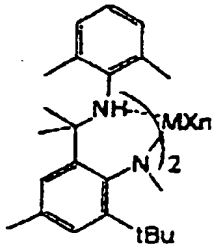


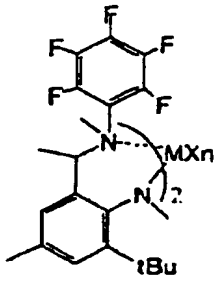



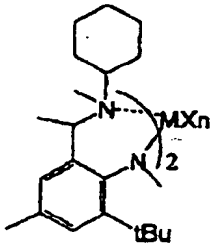



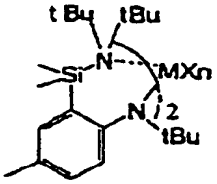



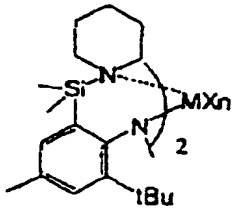



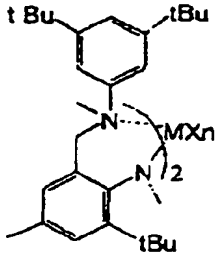



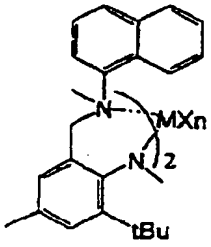



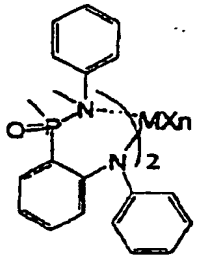



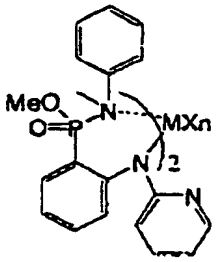



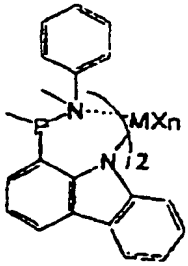



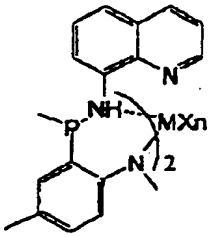



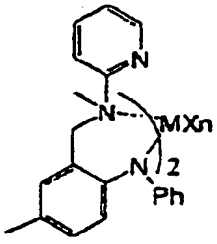



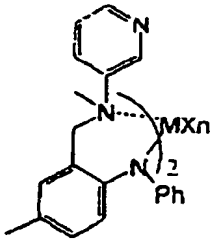



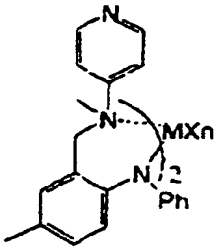



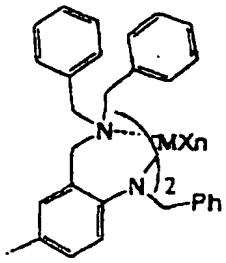



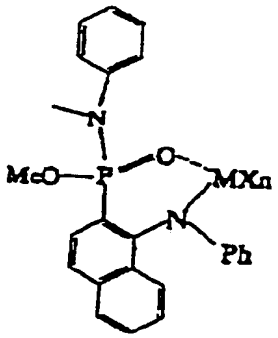
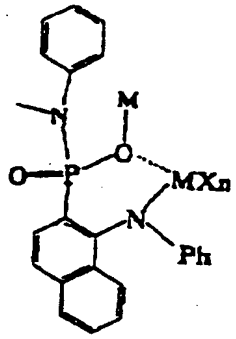
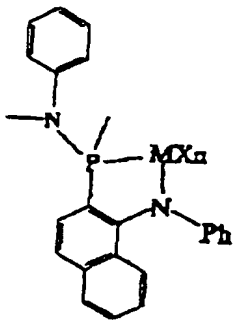
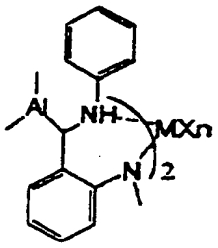
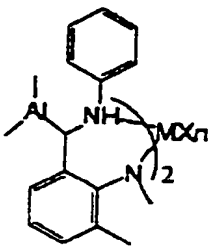
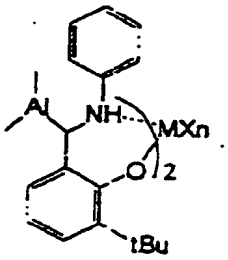
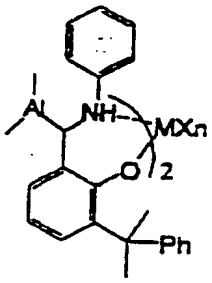
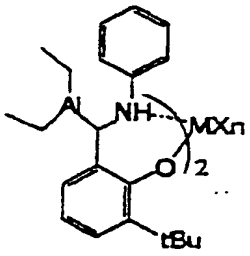
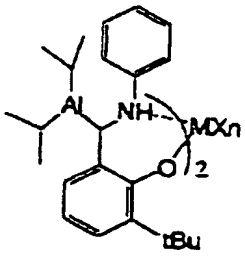
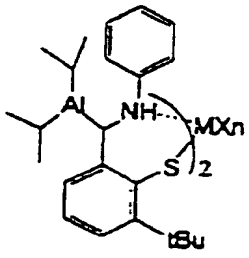



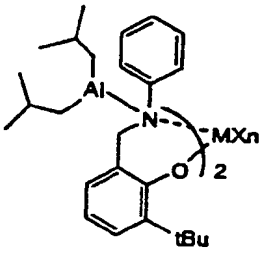
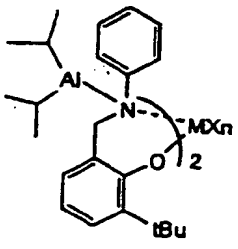
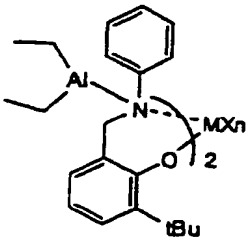
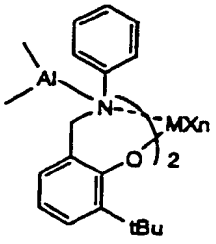



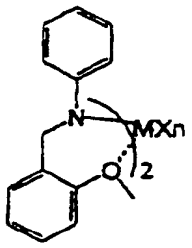



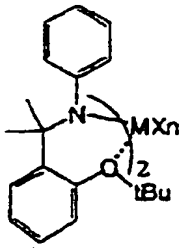











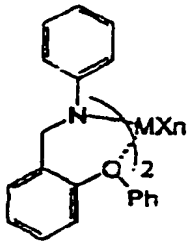





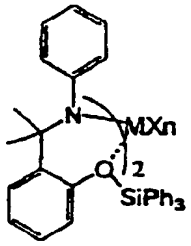
**[0133]** The sixth transition metal compound for use in the invention is a compound represented by the formula (II):

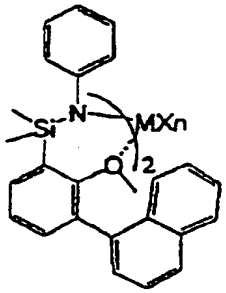
of Zr(IV), and n = 2 in case of Hf(IV).

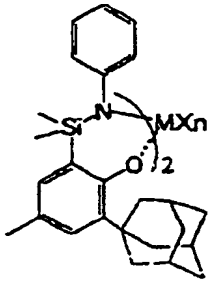


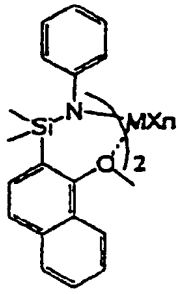



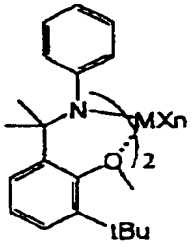



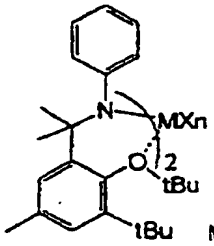



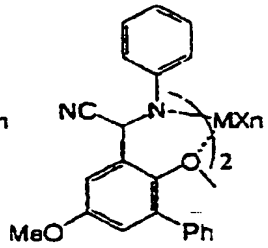



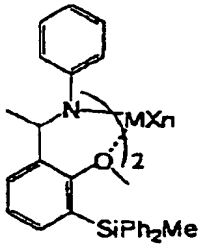



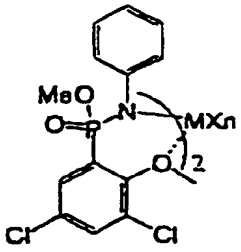



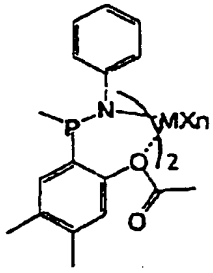



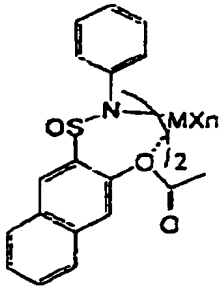



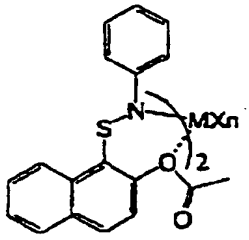



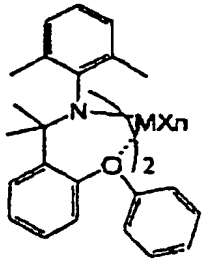



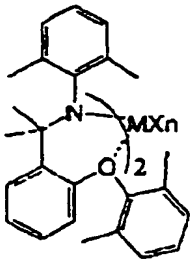



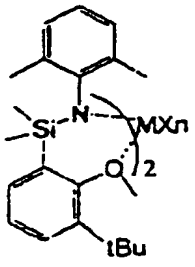



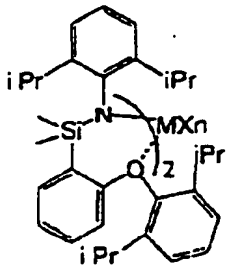



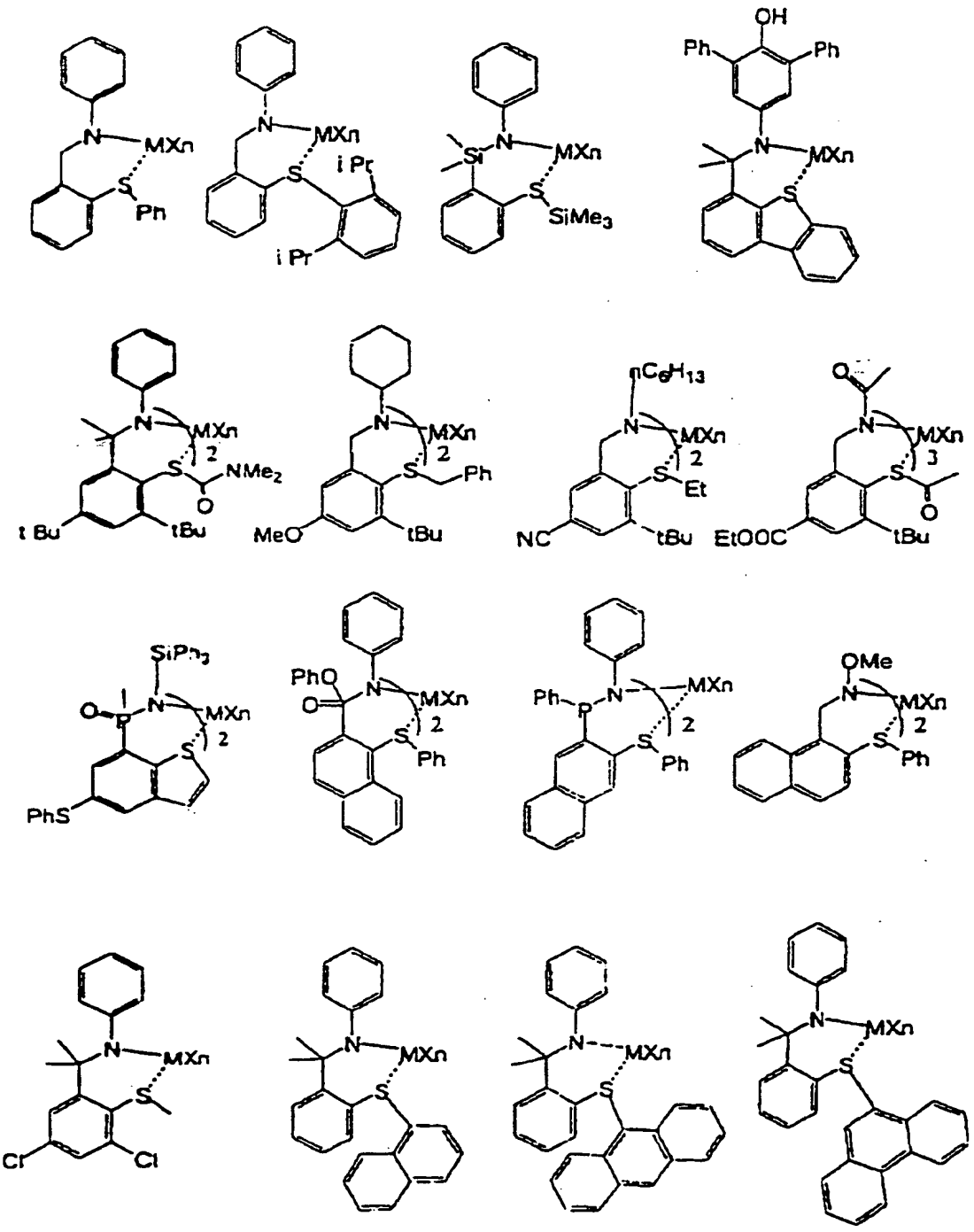



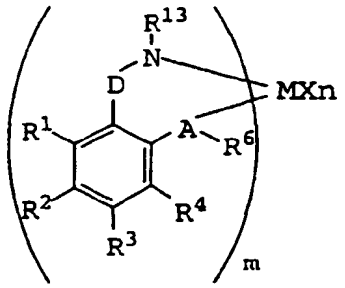







...(III)

**[0148]** In the formula (III), M is a transition metal atom of Group 3 (including lanthanoid) to Group 11 of the periodic table, preferably a metal atom of Group 3 (including lanthanoid) to Group 10, more preferably a metal atom of Group 3 to Group 5 and Group 8 to Group 10, particularly preferably a metal atom of Group 4 or Group 5. Examples of the metal atoms include the same metal atoms as previously described with respect to M in the aforesaid formula (e).

**[0149]** m is an integer of 1 to 3, preferably 1 or 2.

**[0150]** A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$.

**[0151]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and, $-C(R^7)(R^8)-$ is particularly preferable.

**[0152]** $R^1$ to $R^{13}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom. These rings may further have a substituent.

**[0153]** When m is a plural number, one group of $R^1$ to $R^{13}$ contained in one ligand and one group of $R^1$ to $R^{13}$ contained in other ligands may be bonded. $R^1$s, $R^2$s, $R^3$s, $R^4$s, $R^5$s, $R^7$s, $R^8$s, $R^9$s, $R^{10}$s, $R^{11}$s, $R^{12}$s, or $R^{13}$s may be the same or different, respectively. Examples of the groups $R^1$ to $R^{13}$ include the same groups as previously exemplified with respect to $R^1$ to $R^{17}$ in the formula (a).

**[0154]** Examples of the groups D include the same groups as previously exemplified with respect to D in the formula (a).

**[0155]** X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of the groups X include the same groups as previously exemplified with respect to X in the formula (e).

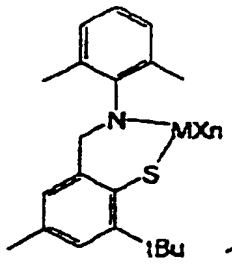
**[0156]** n is a number satisfying a valence of M, specifically an integer of 0 to 5, preferably 1 to 4, more preferably 1 to 3. When n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

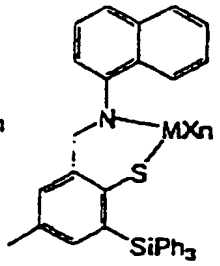
**[0157]** Examples of the transition metal compounds represented by the formula (III) are given below, but not limited thereto.

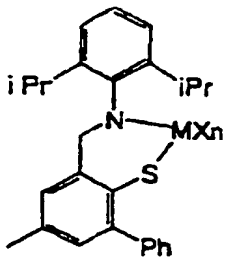
**[0158]** In the following examples, M is a transition metal atom of Group 3 to Group 11 of the periodic table, and particular examples of such metals include scandium, yttrium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, cobalt, rhodium, nickel and palladium. Of these, preferable are scandium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt, rhodium, nickel and palladium. More preferable are titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt and rhodium. Particularly preferable are titanium, zirconium and hafnium.

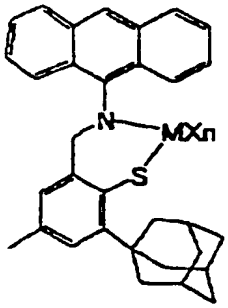
**[0159]** X is halogen such as Cl or Br, or an alkyl group such as methyl, but not limited thereto. When plural X are present, they may be the same or different.

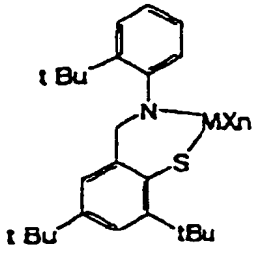
**[0160]** n is decided by a valence of the metal M. For example, when one dianion is bonded to the metal, there can be mentioned n = 0 in case of a divalent metal, n = 1 in case of a trivalent metal, n = 2 in case of a tetravalent metal, and n = 3 in case of a pentavalent metal. More specifically, there can be mentioned n = 2 in case of Ti(IV), n = 2 in case of Zr(IV), n = 2 in case of Hf(IV), n = 0 in case of Co(II), n = 0 in case of Fe(II), n = 0 in case of Rh(II), n = 0 in case of Ni(II), and n = 0 in case of Pd(II).

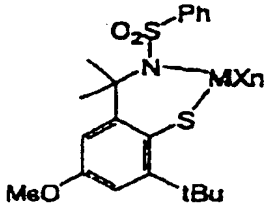


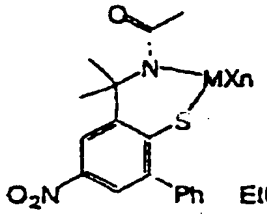



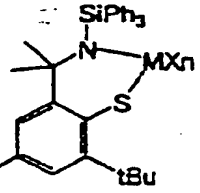



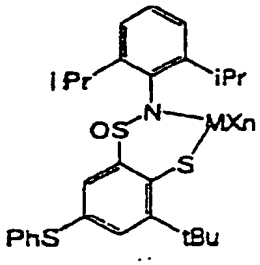



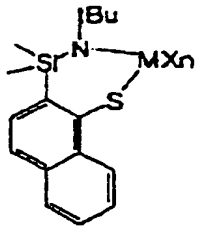



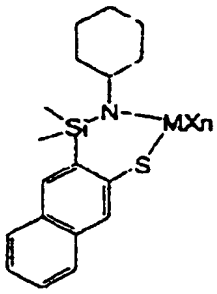



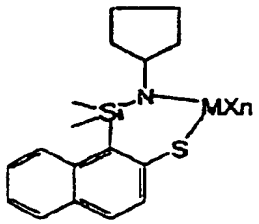



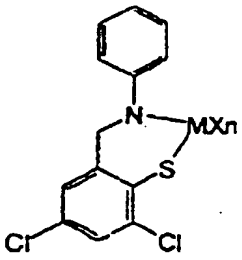



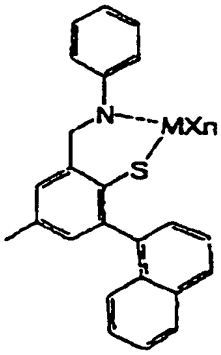



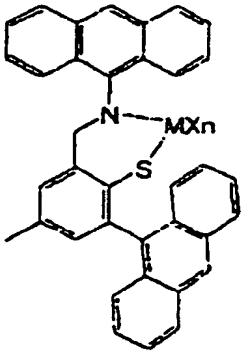



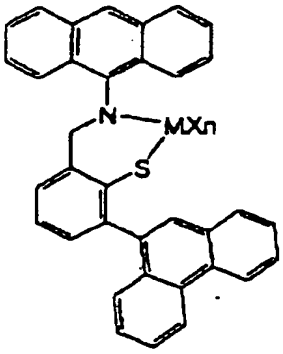



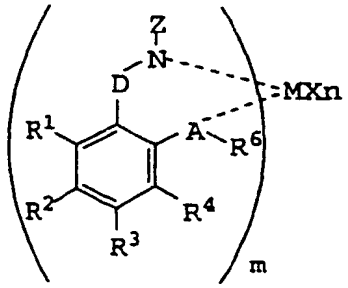





. . . (IV)

wherein the two dotted lines between atoms (A----M and N----M) are used to designate coordinate bonds, but the invention also includes a compound in which one of the bonds is not a coordinate bond.

**[0162]** In the formula (IV), M is a transition metal atom of Group 3 (including lanthanoid) to Group 11 of the periodic table, preferably a metal atom of Group 3 (including lanthanoid) to Group 10, more preferably a metal atom of Group 3 to Group 5 and Group 8 to Group 10, particularly preferably a metal atom of Group 8 to Group 10. Examples of the metal atoms include the same metal atoms as previously described with respect to M in the aforesaid formula (e).

**[0163]** m is an integer of 1 to 6, preferably 1 to 4, more preferably 1 or 2.

**[0164]** A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$.

**[0165]** D is $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, -SO- or -S-. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and $-C(R^7)(R^8)-$ is particularly preferable. When D contains a hetero atom, a coordinate bond may be formed between M and D in the formula (IV).

**[0166]** Z is a bonding group of N and represents $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{17}$. Of these, $-R^{13}$ and $-R^{14}$, or $=C(R^{15})R^{16}$ is preferable.

**[0167]** $R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom. These rings may further have a substituent. It is preferable that any one of $R^6$, $R^{13}$ and $R^{14}$ is an atom or a group other than a hydrogen atom.

**[0168]** When m is a plural number, one group of $R^1$ to $R^{17}$ contained in one ligand and one group of $R^1$ to $R^{17}$ contained in other ligands may be bonded. When $R^{14}$s, $R^{15}$s, $R^{16}$s, or $R^{17}$s are bonded, the main chain hereof is preferably constituted of 3 or more atoms. $R^1$s, $R^2$s, $R^3$s, $R^4$s, $R^5$s, $R^6$s, $R^7$s, $R^8$s, $R^9$s, $R^{10}$s, $R^{11}$s, $R^{12}$s, $R^{13}$s, $R^{14}$s, $R^{15}$s, $R^{16}$s, or $R^{17}$s may be the same or different, respectively. Examples of the groups indicated by $R^1$ to $R^{17}$ include the same groups as previously exemplified with respect to $R^1$ to $R^{17}$ in the formula (a).

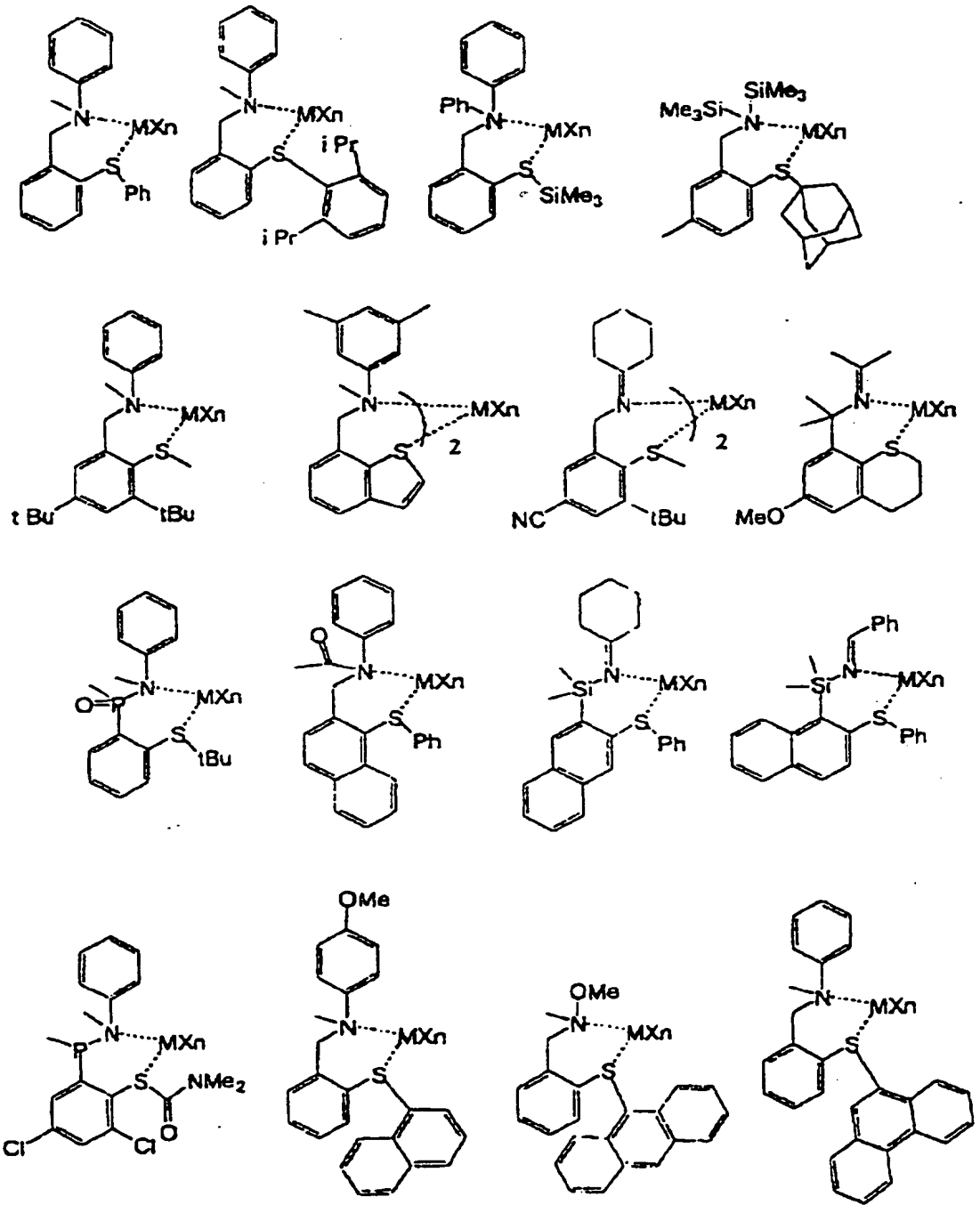
**[0169]** Examples of the groups D include the same groups as previously exemplified with respect to D in the formula (a).

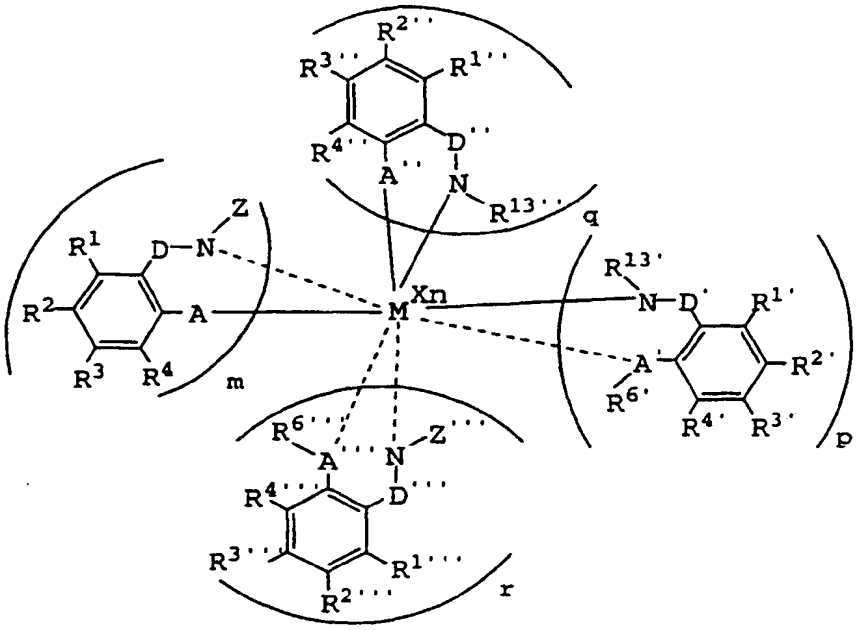
**[0170]** X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of the groups X include the same groups as previously exemplified with respect to X in the formula (e).

**[0171]** n is a number satisfying a valence of M, specifically an integer of 0 to 5, preferably 1 to 4, more preferably 1 to 3. When n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**[0172]** Examples of the transition metal compounds represented by the formula (IV) are given below, but not limited thereto.

**[0173]** In the following examples, M is a transition metal atom of Group 3 to Group 11 of the periodic table, and particular examples of such metals include scandium, yttrium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, cobalt, rhodium, nickel and palladium. Of these, preferable are scandium, lanthanoid, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, ruthenium, cobalt, rhodium, nickel and palladium. More preferable are titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, ruthenium, cobalt, rhodium, nickel and palladium. Particularly preferable are iron, ruthenium, cobalt, rhodium, nickel and palladium.





. . . (V)

wherein the dotted lines between atoms are each used to designate a coordinate bond, but the invention also includes a compound in which the bond N---M adjacent to A-M and the bond A'---M are not coordinate bond, and a compound in which either the bond A'''---M or the bond N---M adjacent thereto is not a coordinate bond.

**[0177]** In the formula (V), M is a transition metal atom of Group 3 (including lanthanoid) to Group 11 of the periodic table, preferably a metal atom of Group 3 (including lanthanoid) to Group 10, more preferably a metal atom of Group 3 to Group 5 and Group 8 to Group 10. Examples of the metal atoms include the same metal atoms as previously described with respect to M in the aforesaid formula (e).

**[0178]** m is an integer of 0 to 6, p is an integer of 0 to 6, q is an integer of 0 to 3, r is an integer of 0 to 6, three or more of them are not 0 at the same time, and they are numbers satisfying the conditions of $m+p+q+r \leq 6$ and $m+p+2q \leq 6$.

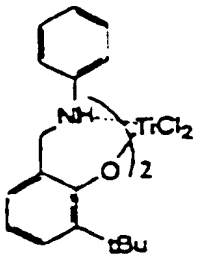
**[0179]** A, A', A'' and A''' may be the same or different and are each an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group $-R^5$ (or $-R^{5'}$, $-R^{5''}$ and $-R^{5'''}$ correspondingly to A', A'' and A''', respectively, and the same shall apply hereinafter).

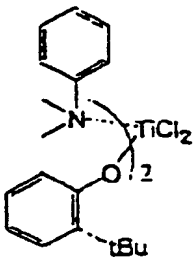
**[0180]** D, D', D'' and D''' may be the same or different and are each $-C(R^7)(R^8)-$, $-Si(R^9)(R^{10})-$, $-P(O)(R^{11})-$, $-P(R^{12})-$, $-SO-$ or $-S-$. Of these, $-C(R^7)(R^8)-$ and $-Si(R^9)(R^{10})-$ are preferable, and $-C(R^7)(R^8)-$ is particularly preferable. When D and D''' contain a hetero atom, a coordinate bond may be formed between M and D and between M and D''' in the formula (V).

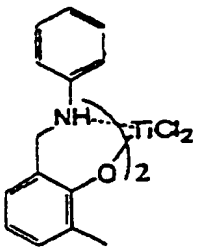
**[0181]** Z and Z''' may be the same or different and are each a bonding group of N, and represent $-R^{13}$ and $-R^{14}$, $=C(R^{15})R^{16}$ or $=NR^{17}$.

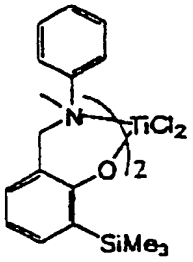
**[0182]** $R^1$ to $R^{17}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom. These rings may further have a substituent. It is preferable that either $R^{13}$ or $R^{14}$, $R^{6'}$, and any one of $R^{6'''}$, $R^{13'''}$ and $R^{14'''}$ are each an atom or a group other than a hydrogen atom.

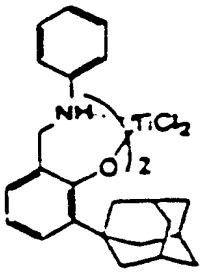
**[0183]** In case of $m+p+q+r \geq 2$, one group of $R^1$ to $R^{17}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ contained in one ligand and one group of $R^1$ to $R^{17}$, $R^{1'}$ to $R^{13'}$, $R^{1''}$ to $R^{13''}$, or $R^{1'''}$ to $R^{17'''}$ contained in other ligands may be bonded. When $R^{13}$s and $R^{13'''}$s, $R^{14}$s and $R^{14'''}$s, $R^{15}$s and $R^{15'''}$s, $R^{16}$s and $R^{16'''}$s, or $R^{17}$s and $R^{17'''}$s are bonded, the main chain of the bond is preferably constituted of 3 or more atoms. Further, $R^1$, $R^{1'}$, $R^{1''}$ and $R^{1'''}$, $R^2$, $R^{2'}$, $R^{2''}$ and $R^{2'''}$, $R^3$, $R^{3'}$, $R^{3''}$ and $R^{3'''}$, $R^4$, $R^{4'}$, $R^{4''}$ and $R^{4'''}$, $R^5$, $R^{5'}$, $R^{5''}$ and $R^{5'''}$, $R^6$, $R^{6'}$, $R^{6''}$ and $R^{6'''}$, $R^7$, $R^{7'}$, $R^{7''}$ and $R^{7'''}$, $R^8$, $R^{8'}$, $R^{8''}$ and $R^{8'''}$, $R^9$, $R^{9'}$, $R^{9''}$ and $R^{9'''}$, $R^{10}$, $R^{10'}$, $R^{10''}$ and $R^{10'''}$, $R^{11}$, $R^{11'}$, $R^{11''}$ and $R^{11'''}$, $R^{12}$, $R^{12'}$, $R^{12''}$ and $R^{12'''}$, $R^{13}$, $R^{13'}$, $R^{13''}$ and

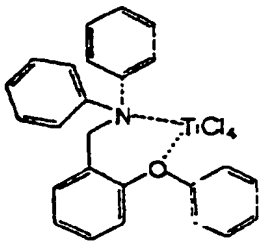


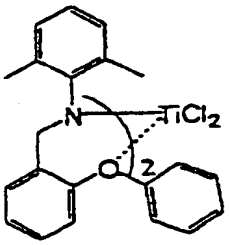



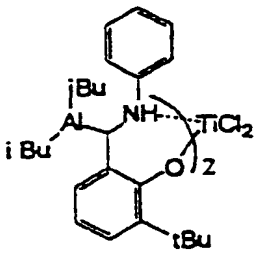



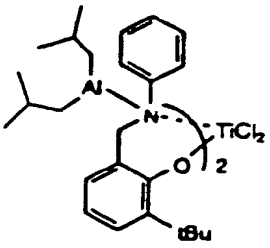



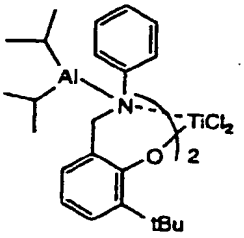



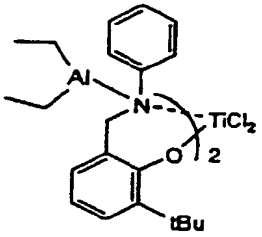



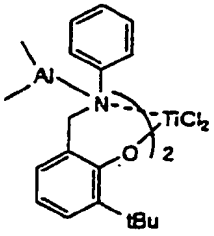



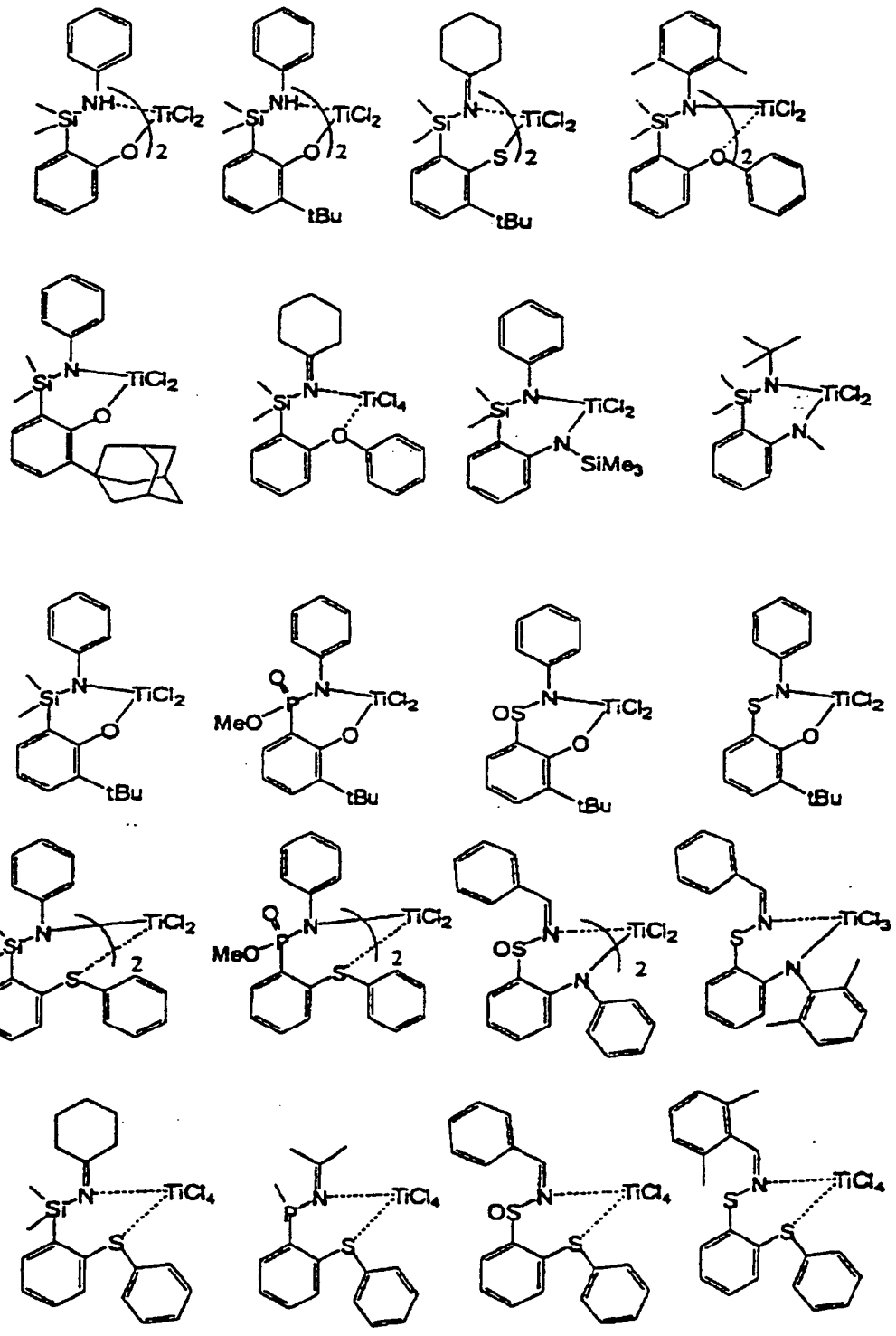



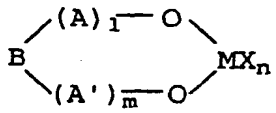


[0192] The transition metal compounds (A) mentioned above are used singly or in combination of two or more kinds.

[0193] The above exemplified compounds wherein the Ti is replaced with Zr or Hf can also be used in the invention.

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. p is an integer of 0 to 4. When p is 2 or greater, plural groups X may be the same or different. X is preferably a halogen atom, a hydrocarbon grope of 1 to 20 carbon atoms or a sulfonato group.

(a-3) Transition metal diphenoxy compound represented by the following formula:



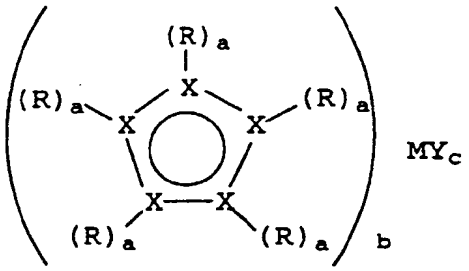
In the above formula, M is a transition metal atom of Group 3 to Group 11 of the periodic table; l and m are each an integer of 0 or 1; and A and A' are each a hydrocarbon group of 1 to 50 carbon atoms, a halogenated hydrocarbon group of 1 to 50 carbon atoms, or a hydrocarbon group or a halogenated hydrocarbon group of 1 to 50 carbon atoms which has a substituent containing oxygen, sulfur or silicon, and A and A' may be the same or different.

B is a hydrocarbon group of 1 to 50 carbon atoms, a halogenated hydrocarbon group of 1 to 50 carbon atoms, a group represented by $R^1R^2Z$ ($R^1$ and $R^2$ are each a hydrocarbon group of 1 to 20 carbon atoms or a hydrocarbon group of 1 to 20 carbon atoms containing at least one hetero atom, and Z is carbon, nitrogen, sulfur, phosphorus or silicon), oxygen or sulfur.

n is a number satisfying a valence of M.

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. When n is 2 or greater, plural groups X may be the same or different or may be bonded to each other to form a ring.

(a-4) Transition metal compound represented by the following formula and comprising a ligand having cyclopentadienyl skeleton containing at least one hetero atom:



In the above formula, M is a transition metal atom of Group 3 to Group 11 of the periodic table.

Each X is an atom of Group 13, Group 14 or Group 15 of the periodic table, and at least one X is an element other than carbon.

Each R may be the same or different and is a hydrogen atom, a halogen atom, a hydrocarbon group, a halogenated hydrocarbon group, a hydrocarbon-substituted silyl group, or a hydrocarbon group substituted with a substituent containing at least one element selected from nitrogen, oxygen, phosphorus, sulfur and silicon. Two or more of R may be bonded to each other to form a ring.

Each a is 0 or 1, and b is an integer of 1 to 4. When b is 2 or greater, the groups $[((R)a)_5\text{-}X_5]$ may be the same or different, and Rs may be bridged to each other.

c is a number satisfying a valence of M.

Y is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. When c is 2 or greater, plural groups Y may be the same or different, and may be bonded to each other to form a ring.

m is an integer of 0 to 3, n is an integer of 0 or 1, p is an integer of 1 to 3, and q is a number satisfying a valence of M.

$R^{41}$ to $R^{48}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group, and two or more of them may be bonded to each other to form a ring.

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. When q is 2 or greater, plural groups X may be the same or different or may be bonded to each other to form a ring.

Y is a group to bridge a boratabenzene ring and is carbon, silicon or germanium.

A is an element of Group 14, Group 15 or Group 16 of the periodic table.

(a-9) Transition metal compound other than the aforesaid compound (a-4) and containing a ligand having cyclopentadienyl skeleton.

(a-10) Compound containing magnesium, titanium and halogen as essential ingredients.

**[0196]** Next, each compound as the component (B), which may optionally be employed in the invention, is described.

(B-1) Organometallic compound

**[0197]** Examples of the organometallic compounds (B-1) optionally employed in the invention include organometallic compounds containing metals of Group 1, Group 2, Group 12 and Group 13 of the periodic table, such as those described below.

(B-1a) Organoaluminum compound represented by the following formula:

$$R^a_m Al(OR^b)_n H_p X_q$$

wherein $R^a$ and $A^b$ may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; X is a halogen atom; and m, n, p and q are numbers satisfying the conditions of $0<m\leq 3$, $0\leq n<3$, $0\leq p<3$, $0\leq q<3$ and $m+n+p+q = 3$.

(B-1b) Alkyl complex compound comprising a metal of Group 1 and aluminum and represented by the following formula:

$$M^2 AlR^a_4$$

wherein $M^2$ is Li, Na or K; and $R^a$ is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms.

(B-1c) Dialkyl compound of a metal of Group 2 or Group 12 and represented by the following formula:

$$R^a R^b M^3$$

wherein $R^a$ and $A^b$ may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; and $M^3$ is Mg, Zn or Cd.

**[0198]** Examples of the organoaluminum compounds (B-1a) include:

an organoaluminum compound represented by the following formula:

$$R^a_m Al(OR^b)_{3-m}$$

wherein $R^a$ and $R^b$ may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; and m is preferably a number satisfying the condition of $1.5\leq m\leq 3$;

an organoaluminum compound represented by the following formula:

$$R^a_m AlX_{3-m}$$

wherein $R^a$ is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; X is a halogen atom; and m is preferably a number satisfying the condition of $0<m<3$;

magnesium chloride, propylmagnesium bromide, propylmagnesium chloride, butylmagnesium bromide, butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium and butylethylmagnesium.

**[0203]** Compounds capable of producing the above-mentioned organoaluminum compounds in the polymerization system, e.g., a combination of halogenated aluminum and alkyllithium and a combination of halogenated aluminum and alkylmagnesium, are also employable.

**[0204]** Of the organometallic compounds (B-1) mentioned above, the organoaluminum compounds are preferable.

**[0205]** The organometallic compounds (B-1) may be used singly or in combination of two or more kinds.

(B-2) Organoaluminum oxy-compound

**[0206]** The organoaluminum oxy-compound (B-2) optionally used in the invention may be conventional aluminoxane and also a benzene-insoluble organoaluminum oxy-compound as exemplified in Japanese Patent Laid-Open Publication No. 78687/1990.

**[0207]** The conventional aluminoxane can be prepared by, for example, the following processes, and is generally obtained as a hydrocarbon solvent solution.

(1) An organoaluminum compound such as trialkylaluminum is added to a hydrocarbon medium suspension of a compound containing adsorption water or a salt containing water of crystallization, e.g., magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate, to allow the organoaluminum compound to react with the adsorption water or the water of crystallization.

(2) Water, ice or water vapor is allowed to directly act on an organoaluminum compound such as trialkylaluminum in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

(3) An organotin oxide such as dimethyltin oxide or dibutyltin oxide is allowed to react with an organoaluminum compound such as trialkylaluminum in a medium such as decane, benzene or toluene.

**[0208]** The aluminoxane may contain a small amount of an organometallic component. Further, it is possible that the solvent or the unreacted organoaluminum compound is distilled off from the recovered solution of aluminoxane and the remainder is redissolved in a solvent or suspended in a poor solvent for aluminoxane.

**[0209]** Examples of the organoaluminum compounds used for preparing the aluminoxane include the same organoaluminum compounds as previously described for the organoaluminum compound (B-1a).

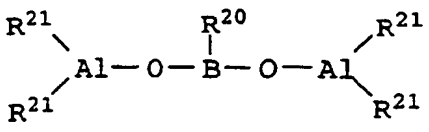
**[0210]** Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable is trimethylaluminum.

**[0211]** The organoaluminum compounds may be used singly or in combination of two or more kinds.

**[0212]** Examples of the solvents used for preparing the aluminoxane include aromatic hydrocarbons, such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons, such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions, such as gasoline, kerosine and gas oil; and halides of these aromatic, aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. Also employable are ethers such as ethyl ether and tetrahydrofuran. Of the solvents, particularly preferable are aromatic hydrocarbons and aliphatic hydrocarbons.

**[0213]** The benzene-insoluble organoaluminum oxy-compound for use in the invention is preferably an organoaluminum oxy-compound containing an Al component which is soluble in benzene at 60 °C in an amount of usually not more than 10 %, preferably not more than 5 %, particularly preferably not more than 2 %, in terms of Al atom. That is, the benzene-insoluble organoaluminum oxy-compound is preferably insoluble or sparingly soluble in benzene.

**[0214]** The organoaluminum oxy-compound employable in the invention is, for example, an organoaluminum oxy-compound containing boron and represented by the following formula (i):



...(i)

wherein $R^{20}$ is a hydrocarbon group of 1 to 10 carbon atoms; and each $R^{21}$ may be the same or different and is a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 10 carbon atoms.

[0229] Examples of the phosphonium cations include triarylphosphonium cations, such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation and tri(dimethylphenyl)phosphonium cation.

[0230] $R^{22}$ is preferably carbonium cation or ammonium cation, particularly preferably triphenylcarbonium cation, N,N-dimethylanilinium cation or N,N-diethylanilinium cation.

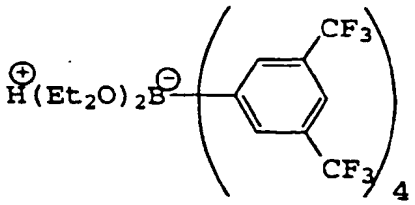
[0231] Also employable as the ionic compounds are a trialkyl-substituted ammonium salt, a N,N-dialkylanilinium salt, a dialkylammonium salt and a triarylphosphonium salt.

[0232] Examples of the trialkyl-substituted ammonium salts include triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron, tri(n-butyl)ammoniumtetra(phenyl)boron, trimethylammoniumtetra(p-tolyl)boron, trimethylammoniumtetra(o-tolyl)boron, tri(n-butyl)ammoniumtetra(pentafluorophenyl)boron, tripropylammoniumtetra(o,p-dimethylphenyl)boron, tri(n-butyl)ammoniumtetra(m,m-dimethylphenyl)boron, tri(n-butyl)ammoniumtetra(p-trifluoromethylphenyl)boron, tri(n-butyl)ammoniumtetra(3,5-ditrifluoromethylphenyl)boron and tri(n-butyl)ammoniumtetra(o-tolyl)boron.

[0233] Examples of the N,N-dialkylanilinium salts include N,N-dimethylaniliniumtetra(phenyl)boron, N,N-diethylaniliniumtetra(phenyl)boron and N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

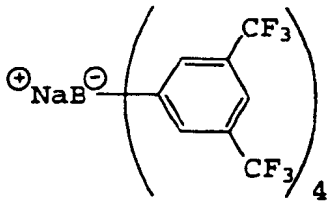
[0234] Examples of the dialkylammonium salts include di(1-propyl)ammoniumtetra(pentafluorophenyl)boron and dicyclohexylammoniumtetra(phenyl)boron.

[0235] Further employable as the ionic compounds are triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate, ferroceniumtetra(pentafluorophenyl)borate, triphenylcarbeniumpentaphenylcyclopentadienyl complex, N,N-diethylaniliniumpentaphenylcyclopentadienyl complex and a boron compound represented by the formula (VII):



...(VII)

wherein Et is an ethyl group, or the formula (VIII):



...(VIII)

[0236] Examples of the borane compounds include:

decaborane(14);
salts of anions, such as bis[tri(n-butyl)ammonium]nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)ammonium] undecaborate, bis[tri(n-butyl)ammonium]dodecaborate, bis[tri(n-butyl)ammonium]decachlorodecaborate and bis[tri(n-butyl)ammonium]dodecachlorododecaborate; and
salts of metallic borane anions, such as tri(n-butyl)ammoniumbis(dodecahydridododecaborate)cobaltate(II I) and bis[tri(n-butyl)ammonium]bis-(dodecahydridododecaborate)nickelate(III).

[0237] Examples of the carborane compounds include:

$Al_2O_3$ as the main component.

**[0245]** The inorganic oxides may contain small amounts of carbonate, sulfate, nitrate and oxide components, such as $Na_2CO_3$, $K_2CO_3$, $CaCO_3$, $MgCO_3$, $Na_2SO_4$, $Al_2(SO_4)_3$, $BaSO_4$, $KNO_3$, $Mg(NO_3)_2$, $Al(NO_3)_3$, $Na_2O$, $K_2O$ and $Li_2O$.

**[0246]** Although the porous oxides differ in their properties depending upon the type and the preparation process thereof, the carrier preferably used in the invention has a particle diameter of 10 to 300 μm, preferably 20 to 200 μm, a specific surface area of 50 to 1,000 $m^2/g$, preferably 100 to 700 $m^2/g$, and a pore volume of 0.3 to 3.0 $cm^3/g$. The carrier may be calcined at 100 to 1,000 °C, preferably 150 to 700 °C, prior to use, if necessary.

**[0247]** Examples of the inorganic chlorides employable in the invention include $MgCl_2$, $MgBr_2$, $MnCl_2$ and $MnBr_2$. In the invention, the inorganic chloride may be used as it is, or may be used after pulverized by, for example, a ball mill or an oscillating mill. The inorganic chloride may also be used as fine particles obtained by dissolving the inorganic chloride in a solvent such as alcohol and then precipitating with a precipitant.

**[0248]** The clay employable as a carrier in the invention is generally constituted mainly of clay minerals. The ion-exchange layered compounds employable as a carrier in the invention are compounds having a crystal structure wherein planes formed by ionic bonding or the like are laminated in parallel to one another with a weak bond strength, and the ions contained therein are exchangeable. Most of clay minerals are ion-exchange layered compounds. The clay, the clay minerals and the ion-exchange layered compounds employable in the invention are not limited to natural ones but include synthetic ones.

**[0249]** Examples of such clay, clay minerals and ion-exchange layered compounds include clay, clay minerals and ion crystalline compounds having layered crystal structures such as hexagonal closest packing type, antimony type, $CdCl_2$ type and $CdI_2$ type.

**[0250]** Particular examples of the clay and the clay minerals include kaolin, bentonite, kibushi clay, gairome clay, allophane, hisingerite, pyrophyllite, mica, montmorillonite, vermiculite, chlorite, palygorskite, kaolinite, nacrite, dickite and halloysite. Particular examples of the ion-exchange layered compounds include crystalline acidic salts of polyvalent metals, such as α-$Zr(HAsO_4)_2 \cdot H_2O$, α-$Zr(HPO_4)_2$, α-$Zr(KPO_4)_2 \cdot 3H_2O$, α-$Ti(HPO_4)_2$, α-$Ti(HAsO_4)_2 \cdot H_2O$, α-$Sn(HPO_4)_2 \cdot H_2O$, γ-$Zr(HPO_4)_2$, γ-$Ti(HPO_4)_2$ and γ-$Ti(NH_4PO_4)_2 \cdot H_2O$.

**[0251]** The clay, the clay minerals and the ion-exchange layered compounds are preferably those having a pore volume, as measured on pores having a radius of not less than 20 Å by a mercury penetration method, of not less than 0.1 cc/g, and are particularly preferably those having a pore volume of 0.3 to 5 cc/g. The pore volume is measured on the pores having a radius of 20 to $3 \times 10^4$ Å by a mercury penetration method using a mercury porosimeter. If the carrier used has a pore volume, as measured on pores having a radius of not less than 20 Å, of less than 0.1 cc/g, high polymerization activity tends to be hardly obtained.

**[0252]** It is also preferable that the clay and the clay minerals to be used in the invention are subjected to chemical treatments. Any of treatments, for example, to remove impurities attached to the surface and to influence the crystal structure of the clay are employable. Examples of such chemical treatments include acid treatment, alkali treatment, salt treatment and organic substance treatment. The acid treatment can contribute to not only removing impurities from the surface but also eluting cations such as Al, Fe and Mg present in the crystal structure to increase the surface area. The alkali treatment can destroy crystal structure of clay to bring about change in the structure of the clay. The salt treatment and the organic substance treatment can produce, for example, ionic composites, molecular composites, or organic derivatives to change the surface area or the distance between layers.

**[0253]** The ion-exchange layered compound for use in the invention may be a layered compound in which the exchangeable ions between layers have been exchanged with other large and bulky ions utilizing ion exchange properties to enlarge the distance between the layers. The bulky ion plays a pillar-like roll to support the layer structure and is generally called a "pillar". Introduction of other substances between layers of a layered compound is called "intercalation". Examples of the guest compounds to be intercalated include cationic inorganic compounds, such as $TiCl_4$ and $ZrCl_4$; metallic alkoxides, such as $Ti(OR)_4$, $Zr(OR)_4$, $PO(OR)_3$ and $B(OR)_3$ (R is a hydrocarbon group or the like); and metallic hydroxide ions, such as $[Al_{13}O_4(OH)_{24}]^{7+}$, $[Zr_4(OH)_{14}]^{2+}$ and $[Fe_3O(OCOCH_3)_6]^+$.

**[0254]** These compounds may be used singly or in combination of two or more kinds.

**[0255]** The intercalation of these compounds may be carried out in the presence of polymers obtained by hydrolysis of metallic alkoxides such as $Si(OR)_4$, $Al(OR)_3$ and $Ge(OR)_4$ (R is a hydrocarbon group or the like) or in the presence of colloidal inorganic compounds such as $SiO_2$. Examples of the pillars include oxides produced by intercalation of the above-mentioned metallic hydroxide ions between layers, followed by dehydration under heating.

**[0256]** The clay, clay minerals and ion-exchange layered compounds mentioned above may be used as they are, or may be used after subjected to a treatment of ball milling, sieving or the like. Moreover, they may be used after subjected to water adsorption or dehydration under heating. The clay, clay minerals and ion-exchange layered compounds may be used singly or in combination of two or more kinds, respectively.

**[0257]** Of the above-mentioned materials, preferable are clay and clay minerals, and particularly preferable are montmorillonite, vermiculite, hectorite, tenorite and synthetic mica.

**[0258]** The organic compound is, for example, a granular or particulate solid compound having a particle diameter of

the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.

(7) A catalyst component wherein the component (B) is supported on the carrier (C), and the component (A) are fed to the polymerization reactor in an arbitrary order.

(8) A catalyst component wherein the component (B) is supported on the carrier (C), the component (A) and the component (B) are fed to the polymerization reactor in an arbitrary order In this case, the components (B) may be the same or different.

(9) A component wherein the component (A) is supported on the carrier (C), and a component wherein the component (B) is supported on the carrier (C) are fed to the polymerization reactor in an arbitrary order.

(10) A component wherein the component (A) is supported on the carrier (C), a component wherein the component (B) is supported on the carrier (C), and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.

(11) The component (A), the component (B) and the organic compound component (D) are fed to the polymerization reactor in an arbitrary order.

(12) A component obtained by previously contacting the component (B) with the component (D), and the component (A) are fed to the polymerization reactor in an arbitrary order.

(13) A component wherein the component (B) and the component (D) are supported on the carrier (C), and the component (A) are fed to the polymerization reactor in an arbitrary order.

(14) A catalyst component obtained by previously contacting the component (A) with the component (B), and the component (D) are fed to the polymerization reactor in an arbitrary order.

(15) A catalyst component obtained by previously contacting the component (A) with the component (B), the component (B) and the component (D) are fed to the polymerization reactor in an arbitrary order.

(16) A catalyst component obtained by previously contacting the component (A) with the component (B), and a component obtained by previously contacting the component (B) with the component (D) are fed to the polymerization reactor in an arbitrary order.

(17) A component wherein the component (A) is supported on the carrier (C), the component (B) and the component (D) are fed to the polymerization reactor in an arbitrary order.

(18) A component wherein the component (A) is supported on the carrier (C), and a component obtained by previously contacting the component (B) with the component (D) are fed to the polymerization reactor in an arbitrary order.

(19) A catalyst component obtained by previously contacting the component (A), the component (B) and the component (D) with one another are fed to the polymerization reactor in an arbitrary order.

(20) A catalyst component obtained by previously contacting the component (A), the component (B) and the component (D) with one another, and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.

(21) A catalyst wherein the component (A), the component (B) and the component (D) are supported on the carrier (C) is fed to the polymerization reactor.

(22) A catalyst component wherein the component (A), the component (B) and the component (D) are supported on the carrier (C), and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.

**[0269]** An olefin may be prepolymerized onto the solid catalyst component wherein the component (A) and optionally the component (B) are supported on the carrier (C).

**[0270]** In the olefin polymerization process according to the invention, an olefin is polymerized or copolymerized in the presence of any of the above-described olefin polymerization catalysts to obtain an olefin polymer.

**[0271]** In the present invention, the polymerization can be carried out as any of livid phase polymerization, such as solution polymerization or suspension polymerization, and gas phase polymerization.

**[0272]** Examples of inert hydrocarbon media for use in the liquid phase polymerization include aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine; alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane; aromatic hydrocarbons, such as benzene, toluene and xylene; halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons. The olefin itself can be used as the solvent.

**[0273]** In the polymerization of an olefin using the olefin polymerization catalyst, the component (A) may be used in an amount of usually $10^{-12}$ to $10^{-2}$ mol, preferably $10^{-10}$ to $10^{-3}$ mol, based on 1 liter of the reaction volume. In the invention, an olefin can be polymerized with a high polymerization activity, even if the component (A) is used in a relatively low concentration.

**[0274]** The component (B-1) may be used in such an amount that the molar ratio of the component (B-1) to the transition metal atom (M) in the component (A) ((B-1)/(M)) becomes usually 0.01 to 100,000, preferably 0.05 to 50,000.

[0288] In the invention, an α-olefin and a polar monomer, for example those described above, can also be copolymerized.

[0289] Further, in the present invention, an α-olefin and a non-conjugated diene or polyene can also be copolymerized. Examples of the non-conjugated dienes and polyenes include 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidene norbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene and 5,9-dimethyl-1,4,8-decatriene.

[0290] Next, a process for preparing the transition metal compound is described.

Process for preparing transition metal compound

[0291] The transition metal compound for use in the invention can be prepared without any specific limitation, for example, by the following process.

[0292] The ligand precursors used are, for example, the compounds of the formulas (a) to (d), and they can be obtained by reacting acylbenzene compounds wherein an oxygen atom, a sulfur atom or a nitrogen atom has been introduced into the o-position with aniline compounds or amine compounds, followed by reduction reaction of the imine moiety or addition reaction such as N-alkylation reaction. For example, when A in the aforesaid formulas is an oxygen atom, the ligand precursor can be synthesized by the following process.

(1) A salicyladlehyde compound or an o-formylaniline compound and a primary amine or an aniline compound having no substituent at the N can be dissolved in a solvent or directly mixed together, and then reacted at room temperature to reflux temperature for about 1 to 48 hours to produce the corresponding imine compound. Examples of the solvents employable herein include alcohols such as methanol and ethanol, and hydrocarbon solvents such as toluene. In the reaction, an acid catalyst such as formic acid, acetic acid or toluenesulfonic acid may be used. During the reaction, the removal of water from the reaction system by Dean and Stark method may be effective to proceed the reaction. Dehydrating agents such as molecular sieves, magnesium sulfate and sodium sulfate may also be used.

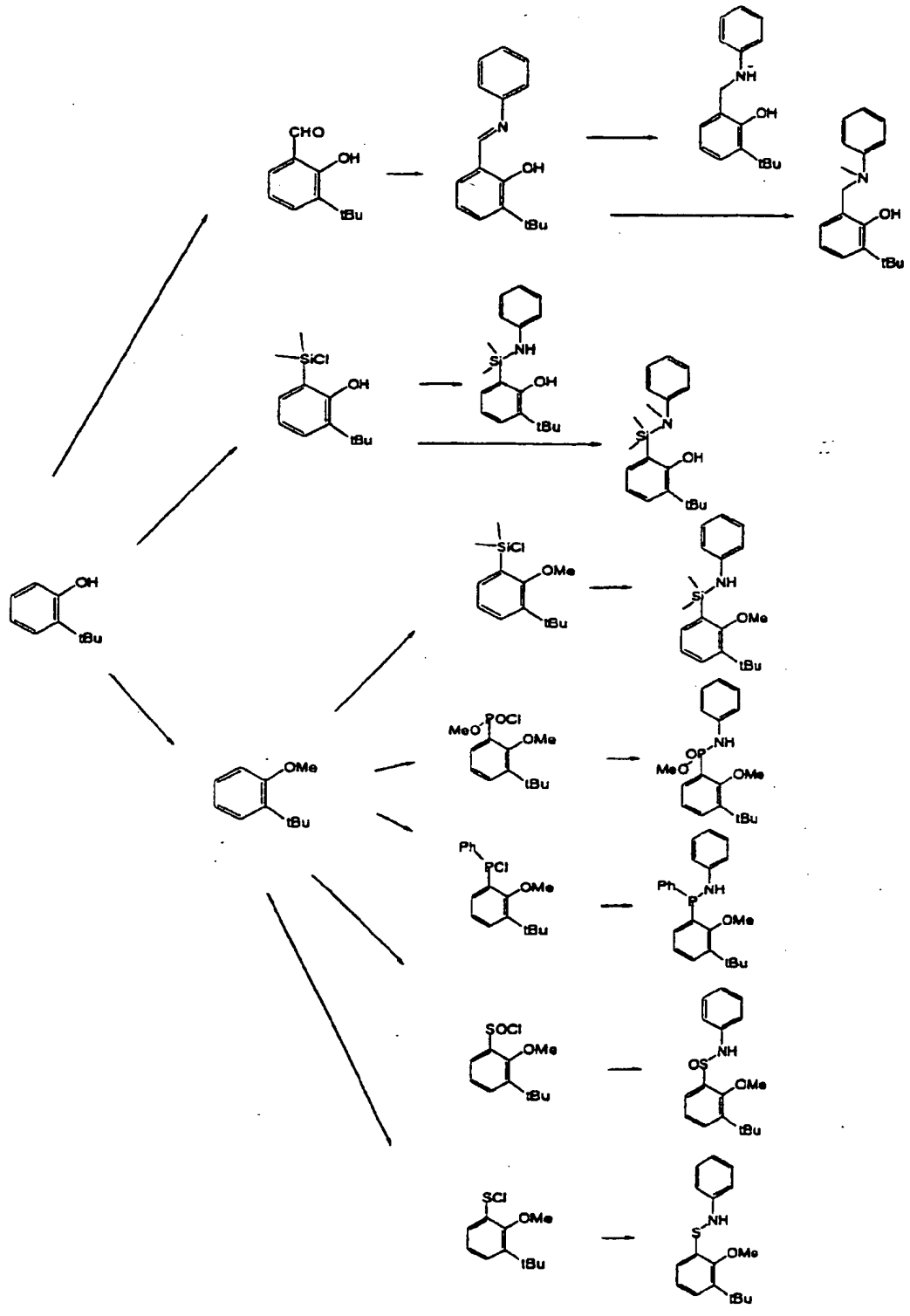
The resulting imine compound can be hydrogenated in the presence of a catalyst such as platinum, or using a hydrogenating agent such as lithium aluminum hydride or diisopropylaluminum, to produce the aforesaid compound (b) or (c) wherein D is -C($R^7$)($R^8$)-. Alternatively, the imine moiety can be subjected to addition reaction such as alkylation using for example an alkyl lithium or a Grignard reagent to produce the aforesaid compound (a) or (d) wherein D is -C($R^7$)($R^8$)-.

(2) Synthesis of Si-containing amine compound: For example, a halogenated silane compound which is obtained by ortho-silylation reaction of a phenolic compound or an aniline compound and which contains a phenyl group having an oxygen-, sulfur- or nitrogen-containing substituent at the o-position to Si, can be reacted with an amine compound or an aniline compound in a similar manner described above, followed by hydrogenation of the imine moiety in a similar manner described above, to produce the aforesaid compound (b) or (c) wherein D is -Si($R^9$)($R^{10}$)-. Alternatively, the imine moiety can be subjected to addition reaction such as alkylation, to produce the aforesaid compound (a) or (d) wherein D is -Si($R^9$)($R^{10}$)-.

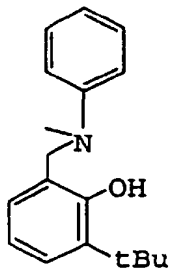
(3) Synthesis of phosphorus-containing amine compound: For example, an oxy-halogenated phosphorus compound which is obtained by oxy-phosphorylation or phosphorylaiton reaction of a phenolic compound or an aniline compound at the o-position and which contains a Phenyl group having an oxygen-, sulfur- or nitrogen-containing substituent at the o-position to PO or P, can be reacted with an amine compound or an aniline compound in a similar manner described above, followed by hydrogenating the imine moiety in a similar manner described above, to produce the aforesaid compound (b) or (c) wherein D is -P(O)($R^{11}$)- or -P($R^{12}$)-. Alternatively, the imine moiety can be subjected to addition reaction such as alkylation, to produce the aforesaid compound (a) or (d) wherein D is -P(O)($R^{11}$)-or -P($R^{12}$)-.

(4) Synthesis of SO-containing amine compound: For example, a halogenated thionyl compound which is obtained by ortho-thionylation of a phenolic compound or an aniline compound and which contains a phenyl group having an oxygen-, sulfur- or nitrogen-containing substituent at the o-position to SO, can be reacted with an amine compound or an aniline compound in a similar manner described above, followed by hydrogenating the imine moiety in a similar manner described above, to produce the aforesaid compound (b) or (c) wherein D is -SO-. Alternatively, the imine moiety can be subjected to addition reaction such as alkylation, to produce the aforesaid compound (a) or (d) wherein D is -SO-.

(5) Synthesis of S-containing amine compound: For example, a phenolic compound or an aniline compound having a halogenated sulfur group at the o-position can be reacted with an amine compound or an aniline compound in a similar manner described above, followed by hydrogenating the imine moiety in a similar manner described above, to produce the aforesaid compound (b) or (c) wherein D is -S-. Alternatively, the imine moiety can be subjected to addition reaction such as alkylation, to produce the aforesaid compound (a) or (d) wherein D is -S-.



[0294] Then, the ligand precursor thus obtained can be reacted with a metal compound (e.g., the compound of the aforesaid formula MXk) to synthesize the corresponding transition metal compound. For example, the compound (a)

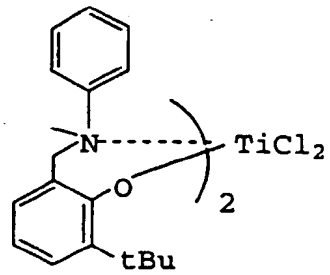


...L1

FD-mass spectrometry: ($M^+$) 269
$^1$H-NMR ($CDCl_3$): 1.42 (s, 9H), 2.76 (s, 3H), 4.33 (s, 2H), 6.75-7.40 (m, 8H), 11.80 (s, 1H)

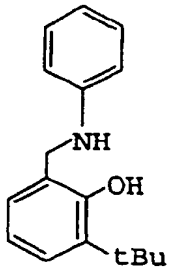
Synthesis of compound (A-1)

**[0305]** To a 100 ml reactor thoroughly dried and purged with argon, 0.40 g (1.50 mmol) of the compound L1 and 10 ml of diethyl ether were introduced, and they were cooled to -78 °C and stirred. To the resulting mixture, 0.98 ml of n-butyllithium (1.60 mmol/ml-n-hexane solution, 1.58 mmol) was dropwise added over a period of 5 minutes, and they were slowly heated to room temperature and stirred at room temperature for 4 hours, to obtain a lithium salt solution. The solution was cooled to -78 °C, and to the solution was slowly dropwise added 1.50 ml of a titanium tetrachloride solution (0.5 mmol/ml-heptane solution, 0.75 mmol). After the dropwise addition, the reaction solution was slowly heated to room temperature with stirring. The reaction solution was further stirred for another 4 hours at room temperature, and the solution was then concentrated under reduced pressure to precipitate a solid. The solid was dissolved in 20 ml of methylene chloride, and insolubles were removed. The filtrate obtained was concentrated under reduced pressure to precipitate a solid. The solid was washed with a mixed solution of diethyl ether and hexane, then further reslurried and washed with hexane, and vacuum dried to obtain 0.06 g (yield: 12 %) of a compound (A-1) of brown powder represented by the following formula.



...A-1

Elemental analysis: Ti: 7.4 % (7.3 %)
(): calculated value
$^1$H-NMR ($CDCl_3$): 1.46 (s, 18H), 3.24 (s, 6H), 4.55 (brs, 4H), 6.50-7.80, 7.25-7.70 (m, 16H)

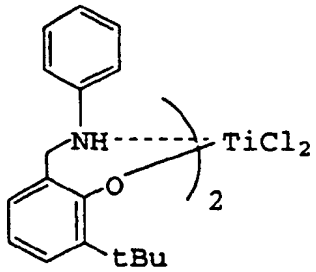



...L2

FD-mass spectrometry: ($M^+$) 255
$^1$H-NMR ($CDCl_3$): 1.42 (s, 9H), 4.13 (s, 2H), 6.75-7.30 (m, 8H)

Synthesis of compound (A-2)

**[0308]** Using L2 synthesized above, a compound (A-2) of orange powder represented by the following formula was synthesized (yield: 7 %) under the same conditions as in Synthesis Example 1.




...A-2

FD-mass spectrometry: ($M^+$) 626
Elemental analysis: Ti: 7.8 % (7.6 %)
(): calculated value

Synthesis Example 4

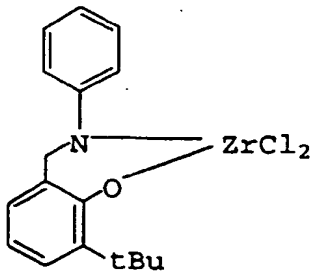
Synthesis of compound (B-2)

**[0309]** Using L2 synthesized in Synthesis Example 3, a compound (B-2) of yellow powder represented by the following formula was synthesized (yield: 10 %) under the same conditions as in Synthesis Example 2.

Synthesis Example 6

Synthesis of compound (B-3)

[0311] Using L2 synthesized in Synthesis Example 3 and $ZrCl_4 \cdot 2THF$, a compound (B-3) of yellow powder represented by the following formula was synthesized (yield: 10 %) under the same conditions as in Synthesis Example 5.




...B-3

FD-mass spectrometry (M+) 414
Elemental analysis Zr: 21.9 % (22.0 %)
(): calculated value

Example 1

[0312] To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the solid phase were saturated with 100 l/hr of ethylene. Then, 0.25 mmol of triisobutylaluminum (TIBA) was added, and subsequently 0.005 mmol of the compound A-1 and 0.006 mmol of triphenylcarbeniumtetrakis(pentafluorophenyl)borate (TrB) were added to initiate polymerization. The reaction was conducted at 25 °C for 30 minutes in an ethylene gas atmosphere at atmospheric pressure. Then, a small amount of isobutanol was added to terminate the polymerization. After the polymerization was completed, the reaction mixture was introduced into a large amount of methanol to precipitate a total amount of a polymer. Then, hydrochloric acid was added, and the mixture was filtered through a glass filter. The resulting polymer was vacuum dried at 80 °C for 10 hours to obtain 0.08 g of polyethylene.

[0313] The polymerization activity per 1 mol of titanium was 32 kg/mol • hr, and the polyethylene had an intrinsic viscosity ($\eta$) of 32.9 dl/g.

Example 2

[0314] To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the solid phase were saturated with 100 l/hr of ethylene. Then, 1.1875 mmol (in terms of aluminum atom) of methylaluminoxane (MAO) was added, and subsequently 0.005 mmol of the compound B-1 obtained in Synthesis Example 1 was added to initiate polymerization. The reaction was conducted at 25 °C for 30 minutes in an ethylene gas atmosphere at atmospheric pressure. Then, a small amount of isobutanol was added to terminate the polymerization. After the polymerization was completed, the reaction mixture was introduced into a large amount of methanol to precipitate a total amount of a polymer. Then, hydrochloric acid was added, and the mixture was filtered through a glass filter. The resulting polymer was vacuum dried at 80 °C for 10 hours to obtain 0.07 g of polyethylene.

[0315] The polymerization activity per 1 mol of zirconium was 28 kg/mol • hr, and the polyethylene had an intrinsic viscosity ($\eta$) of 22.8 dl/g.

Example 3

[0316] Using the compound B-1 obtained in Synthesis Example 2, polymerization reaction was conducted for 30 minutes under the same conditions as in Example 1. As a result, 0.14 g of polyethylene was obtained.

[0317] The polymerization activity per l mol of zirconium was 56 kg/mol • hr, and the polyethylene had an intrinsic vis-

wherein A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group -$R^5$,

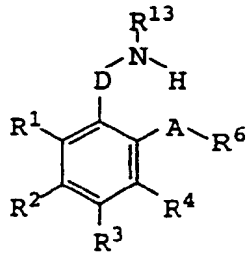
D is -$C(R^7)(R^8)$-, -$Si(R^9)(R^{10})$-, -$P(O)(R^{11})$-, -$P(R^{12})$-, -SO- or -S-,
Z is a bonding group of N and represents -$R^{13}$ and -$R^{14}$, =$C(R^{15})R^{16}$ or =$NR^{17}$, and
$R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring;

$$MXk \qquad (e)$$

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,
k is a number satisfying a valence of M, and
X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group, and when k is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

2. An olefin polymerization catalyst comprising:

(A) a transition metal compound which is obtained by bond-forming reaction of a compound represented by the following formula (b) with a metallic compound represented by the above formula (e) and in which the molar ratio of ligands to metal atoms is in the range of 1 to 6, said ligands being derived from the compound of the formula (b) and bonded to said metal atoms;



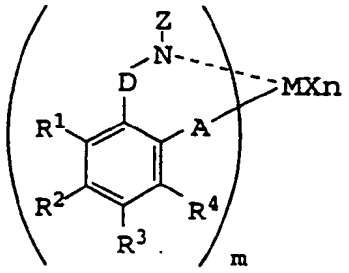
... (b)

wherein A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group -$R^5$,

D is -$C(R^7)(R^8)$-, -$Si(R^9)(R^{10})$-, -$P(O)(R^{11})$-, -$P(R^{12})$-, -SO- or -S-, and
$R^1$ to $R^{13}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, and two or more of them may be bonded to each other to form a ring.

3. An olefin polymerization catalyst comprising:

(A) a transition metal compound which is obtained by bond-forming reaction of a compound represented by the following formula (c) with a metallic compound represented by the above formula (e) and in which the molar ratio of ligands to metal atoms is in the range of 1 to 6, said ligands being derived from the compound of the formula (c) and bonded to said metal atoms;



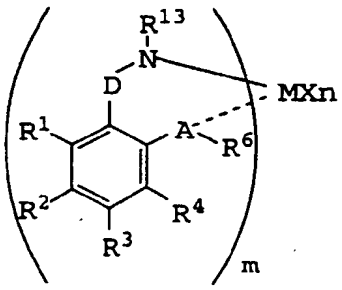
...(I)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 6,
A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group -$R^5$,
D is -$C(R^7)(R^8)$-, -$Si(R^9)(R^{10})$-, -$P(O)(R^{11})$-, -$P(R^{12})$-, -SO- or -S-,
Z is a bonding group of N and represents -$R^{13}$ and -$R^{14}$, =$C(R^{15})R^{16}$ or =$NR^{17}$,
$R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, two or more of them may be bonded to each other to form a ring, and when m is a plural number, one group of $R^1$ to $R^{17}$ contained in one ligand and one group of $R^1$ to $R^{17}$ contained in other ligands may be bonded, and $R^1$s, $R^2$s, $R^3$s, $R^4$s, $R^5$s, $R^7$s, $R^8$s, $R^9$s, $R^{10}$s, $R^{11}$s, $R^{12}$s, $R^{13}$s, $R^{14}$s, $R^{15}$s, $R^{16}$s, or $R^{17}$s may be the same or different, respectively,
n is a number satisfying a valence of M, and
X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group, and when n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**6.** An olefin polymerization catalyst comprising:

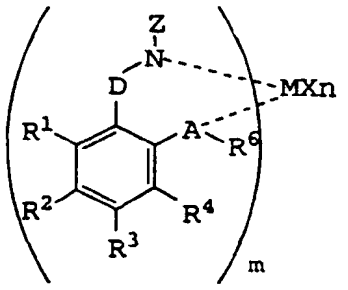
(A) a transition metal compound represented by the following formula (II);



...(II)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 6,
A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group -$R^5$,



. . . (IV)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 6,
A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a bonding group -$R^5$,
D is -C($R^7$)($R^8$)-, -Si($R^9$)($R^{10}$)-, -P(O)($R^{11}$)-, -P($R^{12}$)-, -SO- or -S-,
Z is a bonding group of N and represents -$R^{13}$ and -$R^{14}$, =C($R^{15}$)$R^{16}$ or =N$R^{17}$,
$R^1$ to $R^{17}$ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residual group, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, two or more of them may be bonded to each other to form a ring, and when m is a plural number, one group of $R^1$ to $R^{17}$ contained in one ligand and one group of $R^1$ to $R^{17}$ contained in other ligands may be bonded, and $R^1$s, $R^2$s, $R^3$s, $R^4$s, $R^5$s, $R^6$s, $R^7$s, $R^8$s, $R^9$s, $R^{10}$s, $R^{11}$s, $R^{12}$s, $R^{13}$s, $R^{14}$s, $R^{15}$s, $R^{16}$s, or $R^{17}$s may be the same or different, respectively,
n is a number satisfying a valence of M, and
X is a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residual group, a silicon-containing group, a germanium-containing group or a tin-containing group, and when n is 2 or greater, plural groups X may be the same or different, and may be bonded to each other to form a ring.

**9.** An olefin polymerization catalyst comprising:

(A) a transition metal compound represented by the following formula (V);

(A) is a compound represented by any of the formulas (a) to (d) and (I) to (V) wherein D (including D', D'' and D''' in the formula (V)) is $-C(R^7)(R^8)-$.

11. The olefin polymerization catalyst as claimed in any one of claims 1 to 10, which catalyst further comprises:

(B) at least one compound selected from the group consisting of:

(B-1) an organometallic compound,
(B-2) an organoaluminum oxy-compound, and
(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair.

12. The olefin polymerization catalyst as claimed in any one of claims 1 to 11, which catalyst further comprises a carrier (C).

13. An olefin polymerization process comprising polymerizing or copolymerizing an olefin in the presence of the olefin polymerization catalyst as claimed in any one of claims 1 to 12.

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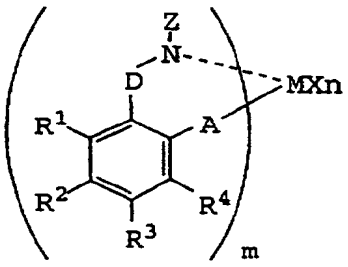
## (54) Olefin polymerization catalyst and polymerization process

(57) An olefin polymerization catalyst having an excellent polymerization activity and an olefin polymerization process using the catalyst are disclosed. The olefin polymerization catalyst comprises (A) a transition metal compound represented by, for example, the following formula (I) and optionally (B) at least one compound selected from an organometallic compound, an organoaluminum oxy-compound and a compound which reacts with the transition metal compound (A) to from an ion pair;




...(I)

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table; m is an integer of 1 to 6; A is -O-, -S-, -Se- or -N(R5)-; D is -C($R^7$)($R^8$)-, -Si($R^9$)($R^{10}$)- or the like; Z is -$R^{13}$ and -$R^{14}$, =C($R^{15}$)$R^{16}$, =N$R^{17}$ or the like; $R^1$ to $R^{17}$ are each H, a hydrocarbon group or the like; n is a number satisfying a valence of M; and X is halogen, a hydrocarbon group or the like.

EP 0 950 667 A3

European Patent Office

Application Number
EP 99 10 6268

## CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

## LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 10 6268

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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09-12-2002

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82